Supporting Information

Useful 1,2-Dioxygenated Dienes: Syntheses and Diels-Alder Reactions en Route to Substituted 2-Naphthols and Phenols

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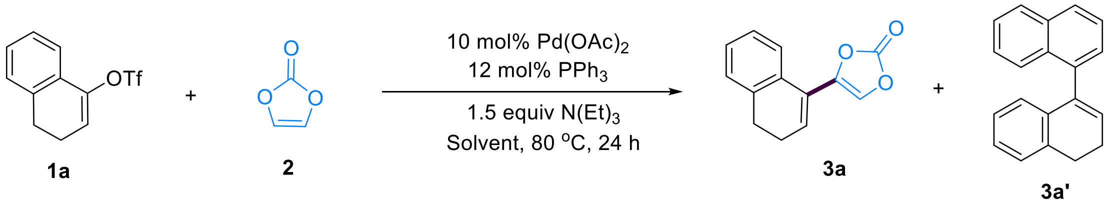
I. General information

All reactions were performed under Argon. The reagents used for experiments were purchased from Adamas, Aladdin, Accela, Sigma-Aldrich, Acros Organics, TCI and Alfa Aesar, and used as received unless otherwise noted. DMF, THF, CH_3CN, Toluene, DMSO and 1,4-Dioxane were distilled from CaH_2 under Argon. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 400 spectrometer. Chemical shifts were reported in the scale relative to TMS (0.00 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. High resolution mass spectroscopy (HRMS) was recorded on a TOF MS mass spectrometer. Column chromatography was carried out on silica gel (200-300 mesh). Starting materials **1a-1d**, **1g and 1j**, **1k-1o, 1r and 1s**,[1] **1e** and **1f**, **1i**, **1u-1v** and **1ae**,[2] **1h**,[3] **1p**,[4] **1q**,[5] **1t**,[6] **1w**,[7] **1x**,[8] **1y and 1ac**,[9] **1z** and **1aa**,[10] **1ab** and **1ad**[11] were prepared according to the reported procedure.

II. Optimization of the reaction conditions

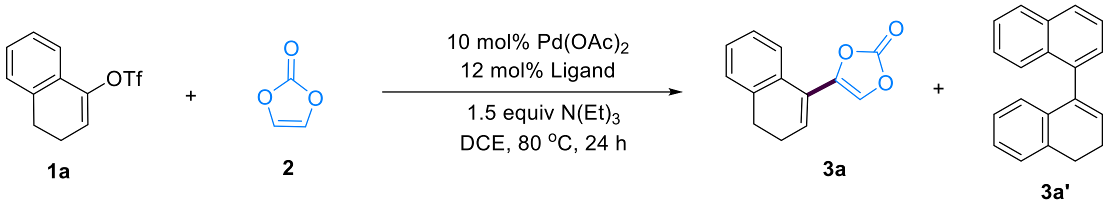
Table S1. Screening of solvent[a]



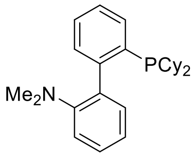
Entry	Solvent	Yield of **3a** (%)[b]	Yield of **3a'** (%)[b]
1	Toluene	24	32
2	DMF	13	18
3	DMSO	12	15
4	CH_3CN	10	21
5	TFE	0	0
6	HFIP	0	0
7	**DCE**	**27**	**27**
8	DCM	14	35
9	THF	24	27
10	1,4-Dioxane	26	30

[a] Reaction conditions: **1a** (0.2 mmol, 0.0556 g), **2** (0.6 mmol, 38 μL), $Pd(OAc)_2$ (10 mol%, 0.0045 g), PPh_3 (12 mol%, 0.0063 g), $N(Et)_3$ (0.3 mmol, 42 μL) and 2 mL of solvent, 80 °C, 24 h. [b] NMR yield using 1,3,5-trimethoxybenzene as the internal standard. DCE = 1,2-Dichloroethane; DMF = *N*,*N*-Dimethylformamide; DMSO = Dimethyl sulfoxide; TFE = 2,2,2-Trifluoroethanol; HFIP = 1,1,1,3,3,3-Hexafluoro-2-propanol; DCM = Dichloromethane; THF = Tetrahydrofuran.

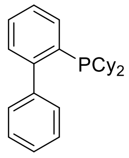
Table S2. Screening of ligand[a]



Entry	Ligand	Yield of **3a** (%)[b]	Yield of **3a'** (%)[b]
1	DavePhos	0	14
2	Rac-BINAP	0	0
3	DPPF	0	26
4	XantPhos	12	0
5	$PCy_3 \cdot HBF_4$	72	10
6	CyJohnPhos	39	0
7	^{t}BuXPhos	13	0



DavePhos



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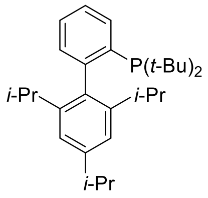
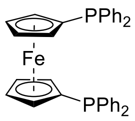
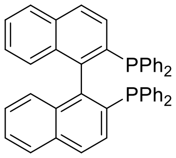


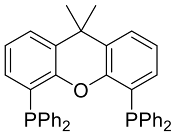
^{t}BuXPhos



DPPF



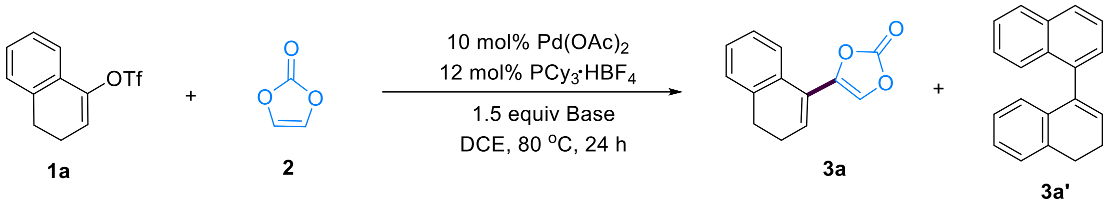
Rac-BINAP



XantPhos

[a] Reaction conditions: **1a** (0.2 mmol, 0.0556 g), **2** (0.6 mmol, 38 μL), $Pd(OAc)_2$ (10 mol%, 0.0045 g), Ligand (12 mol%), $N(Et)_3$ (0.3 mmol, 42 μL) and DCE (2 mL), 80 °C, 24 h. [b]NMR yield using 1,3,5-trimethoxybenzene as the internal standard.

Table S3. Screening of base[a]



Entry	Base	Yield of **3a** (%)[b,c]	Yield of **3a'** (%)[b]
1	DBU	0	0
2	**DIPEA**	**79(75)**	**12**
3	Pyridine	2	0
4	K_2CO_3	28	10
5	Cs_2CO_3	0	0
6	$KHCO_3$	52	7
7	NaOAc	35	3

[a] Reaction conditions: **1a** (0.2 mmol, 0.0556 g), **2** (0.6 mmol, 38 μL), $Pd(OAc)_2$ (10 mol%, 0.0045 g) $PCy_3 \cdot HBF_4$ (12 mol%, 0.0088 g), Base (0.3 mmol) and DCE (2 mL), 80 °C, 24 h. [b]NMR yield using 1,3,5-trimethoxybenzene as the internal standard. [c]Isolated yield given in parentheses. DBU = 1,8-diazabicycloundecene; DIPEA = *N,N*-diisopropylethylamine.

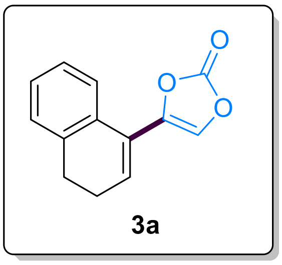
III. General procedure

Condition A: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $Pd(OAc)_2$ (10 mol%, 0.0045 g), $PCy_3{\cdot}HBF_4$ (12 mol%, 0.0088 g), vinyl triflates **1** (0.2 mmol), DIPEA (0.3 mmol, 52 μL), vinylene carbonate (0.6 mmol, 38 μL) and DCE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at a pre-heated 80 °C heating mantle for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **3**.

Condition B: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $Pd(OAc)_2$ (10 mol%, 0.0045 g), $PCy_3{\cdot}HBF_4$ (12 mol%, 0.0088 g), vinyl triflates **1** (0.2 mmol), DIPEA (0.3 mmol, 52 μL), vinylene carbonate (2.0 mmol, 126 μL) and DCE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at a pre-heated 80 °C heating mantle for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **3**.

Condition C: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $Pd(OAc)_2$ (10 mol%, 0.0045 g), PPh_3 (12 mol%, 0.0063 g), vinyl triflates **1** (0.2 mmol), DIPEA (0.3 mmol, 52 μL), vinylene carbonate (2.0 mmol, 126 μL) and DCE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at pre-heated 80 °C heating mantle for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **3**.

IV. Characterization data for the dienes

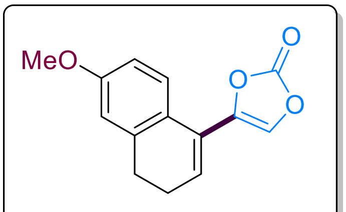


3a

4-(3,4-Dihydronaphthalen-1-yl)-1,3-dioxol-2-one (3a): The title compound was prepared according to the condition A. Yellow oil (32.1 mg, 75%; eluent: 2%-5% ethyl acetate/hexane). ^1H NMR (400 MHz, DMSO) δ 8.04 (s, 1H), 7.39 – 7.30 (m, 1H), 7.28 – 7.21 (m, 3H), 6.54 (t, J = 4.9 Hz, 1H), 2.72 (t, J = 7.9 Hz, 2H), 2.34 (td, J = 7.8, 5.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 152.76, 141.54, 136.66, 131.83, 130.18, 128.58, 128.51, 128.49, 127.20, 124.57, 124.03, 27.13, 22.86. HRMS (ESI): calcd for

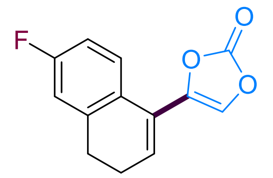
$C_{13}H_{11}O_3$ [M + H]$^+$: 215.0708; found 215.0699.

4-(6-Methoxy-3,4-dihydronaphthalen-1-yl)-1,3-dioxol-2-one (3b): The title compound was prepared according to the condition A. Yellow solid (26.2 mg, 54%; eluent: 2%-15% ethyl acetate/hexane). **m.p.** = 79-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.5 Hz, 1H), 7.16 (s, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.44 (t, *J* = 5.0 Hz, 1H), 3.82 (s, 3H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.36 (td, *J* = 7.8, 5.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.33, 152.63, 142.48, 138.69, 128.89, 126.14, 124.91, 123.51, 123.06, 114.49, 111.28, 55.32, 27.87, 22.83. HRMS (ESI): calcd for $C_{14}H_{13}O_4$ [M + H]$^+$: 245.0814; found 245.0813.



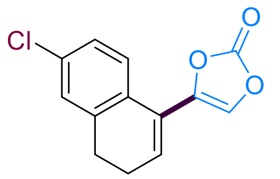
3b

4-(6-Fluoro-3,4-dihydronaphthalen-1-yl)-1,3-dioxol-2-one (3c): The title compound was prepared according to the condition A. Yellow solid (28.8 mg, 62%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 61-62 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.03 (s, 1H), 7.39 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.15 (dd, *J* = 9.4, 2.7 Hz, 1H), 7.05 (td, *J* = 8.7, 2.8 Hz, 1H), 6.51 (t, *J* = 4.9 Hz, 1H), 2.75 (t, *J* = 7.9 Hz, 2H), 2.34 (td, *J* = 7.8, 5.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 161.92 (d, *J* = 245.6 Hz), 152.73, 141.43, 139.86 (d, *J* = 8.0 Hz), 131.32, 128.65, 126.76 (d, *J* = 3.1 Hz), 126.63 (d, *J* = 8.6 Hz), 123.29, 115.56 (d, *J* = 21.8 Hz), 113.52 (d, *J* = 21.2 Hz), 27.12, 22.49. ^{19}F NMR (377 MHz, DMSO) δ -113.50. HRMS (ESI): calcd for $C_{13}H_{10}FO_3$ [M + H]$^+$: 233.0614; found 233.0610.



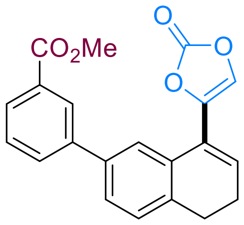
3c

4-(6-Chloro-3,4-dihydronaphthalen-1-yl)-1,3-dioxol-2-one (3d): The title compound was prepared according to the condition A. Yellow oil (27.4 mg, 55%; eluent: 2%-10% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 8.03 (s, 1H), 7.37 (d, *J* = 5.8 Hz, 1H), 7.36 (s, 1H), 7.29 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.56 (t, *J* = 4.9 Hz, 1H), 2.74 (t, *J* = 7.9 Hz, 2H), 2.35 (td, *J* = 7.8, 5.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 152.71, 141.22, 139.17, 132.73, 132.48, 129.09, 128.69, 128.29, 126.95, 126.30, 123.24, 26.77, 22.58. HRMS (ESI): calcd for $C_{13}H_{10}ClO_3$ [M + H]$^+$: 249.0318; found 249.0308.



3d

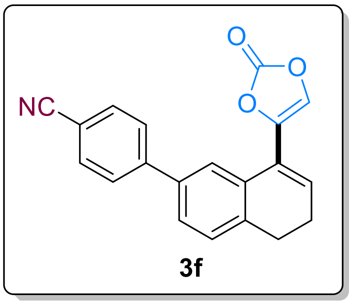
Methyl 3-(8-(2-oxo-1,3-dioxol-4-yl)-5,6-dihydronaphthalen-2-yl)benzoate (3e): The title compound was prepared according to the condition B. Yellow oil (36.8 mg, 53%; eluent: 2%-10% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 8.19 (t, *J* = 1.5 Hz, 1H), 8.14 (s, 1H), 8.01 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.61 (m, 1H), 7.59 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 6.61 (t, *J* = 4.9 Hz, 1H), 3.91 (s, 3H), 2.81 (dd, *J* = 16.8, 9.2 Hz, 2H), 2.40 (dt, *J* = 12.7, 6.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 166.66, 152.85, 141.42, 140.98, 138.32, 136.55,



3e

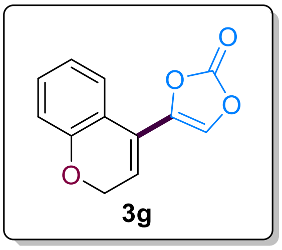
132.42, 132.25, 130.97, 130.74, 129.84, 129.24, 128.76, 128.46, 127.67, 127.02, 124.07, 122.95, 52.70, 26.86, 22.84. HRMS (ESI): calcd for $C_{21}H_{17}O_5$ $[M + H]^+$: 349.1076; found 349.1075.

4-(8-(2-Oxo-1,3-dioxol-4-yl)-5,6-dihydronaphthalen-2-yl)benzonitrile (3f): The title compound was prepared according to the condition B. Light yellow solid (25.8 mg, 41%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 149-150 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.14 (s, 1H), 7.91 (s, 4H), 7.64 (d, *J* = 3.1 Hz, 1H), 7.61 (s, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 6.60 (t, *J* = 4.8 Hz, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.38 (dd, *J* = 12.7, 7.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 152.85, 144.84, 141.31, 137.44, 133.16, 132.56, 131.05, 129.31, 128.80, 128.13, 127.21, 123.96, 123.08, 119.38, 110.40, 26.87, 22.79. HRMS (ESI): calcd for $C_{20}H_{14}NO_3$ $[M + H]^+$: 316.0974; found 316.0966.



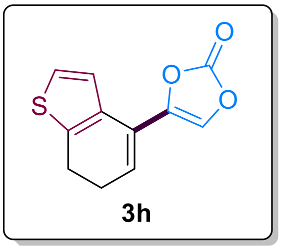
3f

4-(2*H*-chromen-4-yl)-1,3-dioxol-2-one (3g): The title compound was prepared according to the condition A. Light yellow solid (24.3 mg, 56%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 56-57 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.18 (s, 1H), 7.35 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.27 (td, *J* = 7.9, 1.4 Hz, 1H), 7.00 (td, *J* = 7.6, 1.0 Hz, 1H), 6.94 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.35 (t, *J* = 4.3 Hz, 1H), 4.79 (d, *J* = 4.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.49, 152.41, 139.59, 130.66, 129.46, 125.02, 124.36, 122.27, 120.86, 119.23, 117.03, 64.62. HRMS (ESI): calcd for $C_{12}H_9O_4$ $[M + H]^+$: 217.0501; found 217.0493.



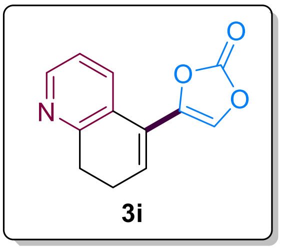
3g

4-(6,7-Dihydrobenzo[*b*]thiophen-4-yl)-1,3-dioxol-2-one (3h): The title compound was prepared according to the condition B. Yellow oil (18.0 mg, 41%; eluent: 2%-10% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 8.12 (s, 1H), 7.40 (d, *J* = 5.2 Hz, 1H), 7.17 (d, *J* = 5.2 Hz, 1H), 6.29 (t, *J* = 4.9 Hz, 1H), 2.85 (t, *J* = 8.7 Hz, 2H), 2.53 – 2.49 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 152.55, 141.33, 137.42, 129.85, 127.79, 125.39, 124.28, 123.20, 120.89, 23.85, 22.03. HRMS (ESI): calcd for $C_{11}H_9O_3S$ $[M + H]^+$: 221.0272; found 221.0266.



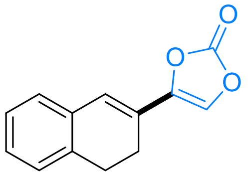
3h

4-(7,8-Dihydroquinolin-5-yl)-1,3-dioxol-2-one (3i): The title compound was prepared according to the condition A. Brown solid (28.0 mg, 65%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 80-81 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.37 (dd, *J* = 4.8, 1.1 Hz, 1H), 8.08 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.26 (dd, *J* = 7.8, 4.9 Hz, 1H), 6.59 (t, *J* = 4.9 Hz, 1H), 2.89 (t, *J* = 8.1 Hz, 2H), 2.50 (td, *J* = 8.0, 5.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 157.08, 152.64, 148.29, 140.81, 132.70, 131.57, 128.76, 125.64, 122.85, 122.50, 29.89, 22.80. HRMS (ESI): calcd for $C_{12}H_{10}NO_3$ $[M + H]^+$: 216.0661; found 216.0658.



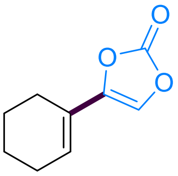
3i

4-(3,4-Dihydronaphthalen-2-yl)-1,3-dioxol-2-one (3j): The title compound was prepared according to the condition B. Light yellow solid (22.6 mg, 53%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 99-100 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.05 (s, 1H), 7.28 – 7.23 (m, 1H), 7.20 (d, *J* = 5.9 Hz, 1H), 7.19 (s, 2H), 6.82 (s, 1H), 2.84 (t, *J* = 8.1 Hz, 2H), 2.39 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 152.70, 143.11, 135.37, 132.96, 128.55, 128.52, 127.97, 127.76, 127.25, 124.17, 122.52, 26.77, 21.81. HRMS (ESI): calcd for $C_{13}H_{11}O_3$ [M + H]$^+$: 215.0708; found 215.0705.



3j

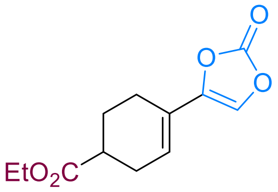
4-(Cyclohex-1-en-1-yl)-1,3-dioxol-2-one (3k): The title compound was prepared according to the condition A. Light yellow solid (25.8 mg, 77%; eluent: 2%-5% ethyl acetate/hexane). **m.p.** = 58-59 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.74 (s, 1H), 6.08 (t, *J* = 3.9 Hz, 1H), 2.19 – 2.11 (m, 2H), 2.07 – 2.01 (m, 2H), 1.68 – 1.55 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 152.86, 143.80, 126.57, 126.11, 122.43, 24.89, 22.99, 21.85, 21.54. HRMS (ESI): calcd for $C_9H_{11}O_3$ [M + H]$^+$: 167.0708; found 167.0699.



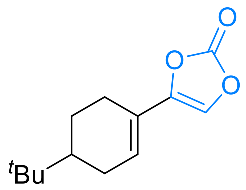
3k

Gram scale procedure: A 250 mL round bottomed flask equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, $Pd(OAc)_2$ (10 mol%, 0.112 g), $PCy_3{\cdot}HBF_4$ (12 mol%, 0.221 g), **1k** (5.0 mmol, 1.15 g), DIPEA (7.5 mmol, 1.3 mL), vinylene carbonate (15.0 mmol, 0.95 mL) and DCE (50 mL) was added. After the connection of a reflux condenser, the flask was evacuated and refilled with Argon for three times and the reaction mixture was heated in a preheated 80 °C oil bath for 24 hours under Argon balloon. Up completion, the reaction mixture was diluted with ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide **3k** (658 mg, 79%).

Ethyl 4-(2-oxo-1,3-dioxol-4-yl)cyclohex-3-ene-1-carboxylate (3l): The title compound was prepared according to the condition A. Light yellow solid (26.8 mg, 56%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 78-79 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.77 (s, 1H), 6.07 (d, *J* = 0.8 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 2.62 (tdd, *J* = 10.6, 5.6, 3.1 Hz, 1H), 2.48 – 2.38 (m, 1H), 2.36 – 2.25 (m, 1H), 2.14 (d, *J* = 4.8 Hz, 2H), 2.01 (ddd, *J* = 12.0, 7.6, 4.1 Hz, 1H), 1.65 (ddt, *J* = 13.1, 10.8, 7.9 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 174.66, 152.77, 143.35, 126.52, 124.73, 122.06, 60.48, 38.20, 27.23, 24.15, 22.20, 14.51. HRMS (ESI): calcd for $C_{12}H_{15}O_5$ [M + H]$^+$: 239.0919; found 239.0913.

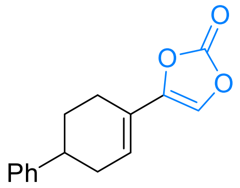


3l



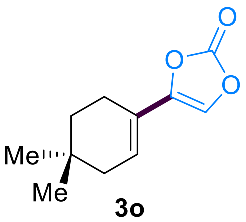
3m

4-(4-(*Tert*-butyl)cyclohex-1-en-1-yl)-1,3-dioxol-2-one (3m): The title compound was prepared according to the condition A. Light yellow solid (35.4 mg, 80%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 80-81 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.25 – 6.22 (m, 1H), 2.25 (dd, *J* = 14.4, 10.1 Hz, 1H), 2.15 – 2.08 (m, 2H), 2.00 – 1.94 (m, 1H), 1.93 – 1.88 (m, 1H), 1.39 – 1.31 (m, 1H), 1.31 – 1.26 (m, 1H), 0.89 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.89, 144.43, 128.30, 123.43, 121.45, 43.66, 32.25, 27.10, 26.80, 24.52, 23.01. HRMS (ESI): calcd for $C_{13}H_{19}O_3$ $[M + H]^+$: 223.1334; found 223.1325.



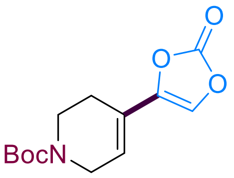
3n

4-(1,2,3,6-Tetrahydro-[1,1'-biphenyl]-4-yl)-1,3-dioxol-2-one (3n): The title compound was prepared according to the condition A. Light yellow solid (30.3 mg, 63% eluent: 2%-5% ethyl acetate/hexane). **m.p.** = 78-79 ºC. ^{1}H NMR (400 MHz, DMSO) δ 7.79 (s, 1H), 7.34 – 7.24 (m, 4H), 7.23 – 7.18 (m, 1H), 6.24 – 6.07 (m, 1H), 2.87 – 2.72 (m, 1H), 2.49 – 2.39 (m, 1H), 2.27 (dd, *J* = 8.4, 7.2 Hz, 1H), 2.20 (dd, *J* = 23.2, 6.9 Hz, 2H), 1.98 – 1.90 (m, 1H), 1.82 – 1.71 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 152.87, 146.34, 143.65, 128.81, 127.15, 126.62, 126.39, 126.24, 122.26, 39.25, 33.00, 28.75, 23.73. HRMS (ESI): calcd for $C_{15}H_{15}O_3$ $[M + H]^+$: 243.1021; found 243.1010.



3o

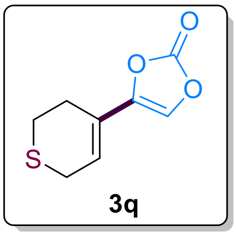
4-(4,4-Dimethylcyclohex-1-en-1-yl)-1,3-dioxol-2-one (3o): The title compound was prepared according to the condition A. Light yellow solid (18.6 mg, 48%; eluent: 2%-5% ethyl acetate/hexane). **m.p.** = 56-57 ºC. ^{1}H NMR (400 MHz, DMSO) δ 7.75 (s, 1H), 6.03 (t, *J* = 4.1 Hz, 1H), 2.07 (ddd, *J* = 8.3, 4.3, 1.9 Hz, 2H), 1.99 – 1.93 (m, 2H), 1.42 (t, *J* = 6.5 Hz, 2H), 0.91 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 152.85, 143.66, 126.15, 125.68, 121.22, 38.76, 34.20, 28.69, 28.29, 20.85. HRMS (ESI): calcd for $C_{11}H_{15}O_3$ $[M + H]^+$: 195.1021; found 195.1011.



3p

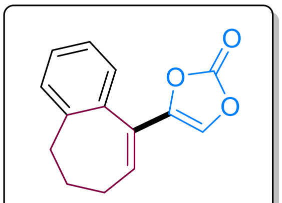
Tert-butyl 4-(2-oxo-1,3-dioxol-4-yl)-3,6-dihydropyridine-1(2H)-carboxylate (3p): The title compound was prepared according to the condition A. Light yellow solid (34.3 mg, 65%; eluent: 10%-20% ethyl acetate/hexane). **m.p.** = 114-115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.15 (s, 1H), 4.09 (d, *J* = 2.4 Hz, 2H), 3.59 (t, *J* = 5.7 Hz, 2H), 2.20 (s, 2H), 1.48 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.58, 152.37, 143.24, 124.50, 123.55, 120.51, 80.19, 43.42, 38.63, 28.40, 23.27. HRMS (ESI): calcd for $C_{13}H_{18}NO_5$ $[M + H]^+$: 268.1185; found 268.1178.

4-(3,6-Dihydro-2H-thiopyran-4-yl)-1,3-dioxol-2-one (3q): The title compound was prepared according to the condition B. Light yellow solid (22.1 mg, 60%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 60-61 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.84 (s, 1H), 6.25 (t, J = 4.4 Hz, 1H), 3.33 – 3.29 (m, 2H), 2.78 (t, J = 5.8 Hz, 2H), 2.38 – 2.28 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 152.66, 143.56, 126.84, 123.41, 123.17, 24.88, 23.98, 23.61. HRMS (ESI): calcd for $C_8H_9O_3S$ $[M + H]^+$: 185.0272; found 185.0418.



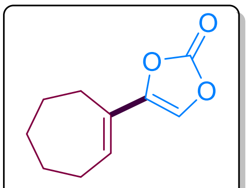
3q

4-(6,7-Dihydro-5H-benzo[7]annulen-9-yl)-1,3-dioxol-2-one (3r): The title compound was prepared according to the condition A. Yellow oil (31.6 mg, 69%; eluent: 2%-5% ethyl acetate/hexane). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 – 7.15 (m, 4H), 6.73 (s, 1H), 6.57 (t, J = 7.6 Hz, 1H), 2.51 (t, J = 7.0 Hz, 2H), 2.08 (p, J = 7.1 Hz, 2H), 1.91 (q, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 152.69, 143.42, 141.78, 134.13, 130.69, 129.46, 128.55, 127.05, 126.44, 126.39, 125.83, 34.38, 31.73, 24.33. HRMS (ESI): calcd for $C_{14}H_{13}O_3$ $[M + H]^+$: 229.0865; found 229.0856.



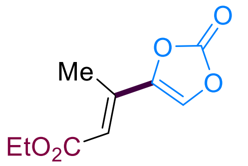
3r

4-(Cyclohept-1-en-1-yl)-1,3-dioxol-2-one (3s): The title compound was prepared according to the condition A. Light yellow solid (19.3 mg, 54%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 38-39 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.86 (s, 1H), 6.25 (t, J = 6.8 Hz, 1H), 2.30 – 2.25 (m, 2H), 2.25 – 2.21 (m, 2H), 1.78 – 1.71 (m, 2H), 1.53 – 1.43 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 152.95, 144.34, 131.30, 128.80, 126.57, 31.92, 28.18, 27.55, 26.44, 26.38. HRMS (ESI): calcd for $C_{10}H_{13}O_3$ $[M + H]^+$: 181.0865; found 181.0855.



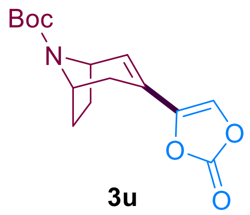
3s

Ethyl (*E*)-3-(2-oxo-1,3-dioxol-4-yl)but-2-enoate (3t): The title compound was prepared according to the condition A. Light yellow solid (9.9 mg, 25%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 60-61 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.32 (s, 1H), 5.98 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 2.22 (d, J = 1.0 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 165.57, 152.03, 143.08, 137.13, 132.82, 115.39, 60.47, 14.53, 13.18. HRMS (ESI): calcd for $C_9H_{11}O_5$ $[M + H]^+$: 199.0606; found 199.0599.

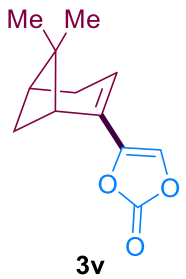


3t

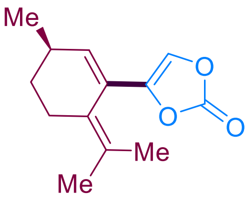
Tert-butyl (1*R*,5*S*)-3-(2-oxo-1,3-dioxol-4-yl)-8-azabicyclo[3.2.1]oct-2-ene-8-carboxylate (3u): The title compound was prepared according to the condition A. Light yellow solid (33.5 mg, 57%; eluent: 10%-20% ethyl acetate/hexane). **m.p.** = 116-117 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.89 (s, 1H), 6.47 (s, 1H), 4.49 (s, 2H), 2.87 (s, 1H), 2.24 (d, J = 9.1 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.97 – 1.90 (m, 1H), 1.81 (d, J = 16.4 Hz, 1H), 1.70 – 1.60 (m, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.73, 152.33, 143.19, 131.28, 124.63, 119.23, 79.95, 53.15, 50.93, 34.21, 31.59, 29.24, 28.37. HRMS (ESI): calcd for $C_{15}H_{20}NO_5$ $[M + H]^+$: 294.1341; found 294.1345.



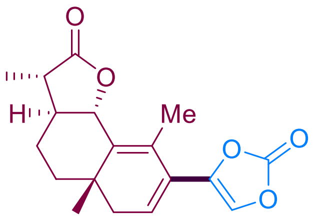
3u


3v

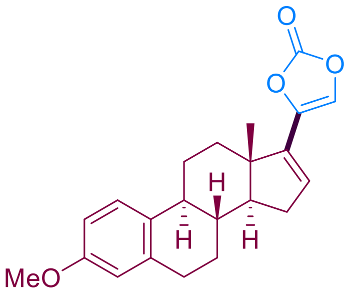
4-((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-1,3-dioxol-2-one (3v): The title compound was prepared according to the condition B. Yellow oil (19.6 mg, 48%; eluent: 2%-5% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 7.84 (s, 1H), 5.93 (s, 1H), 2.50 – 2.47 (m, 1H), 2.44 (dd, *J* = 6.7, 3.6 Hz, 1H), 2.39 (t, *J* = 2.7 Hz, 1H), 2.35 – 2.31 (m, 1H), 2.17 – 2.12 (m, 1H), 1.32 (s, 3H), 1.16 (d, *J* = 8.9 Hz, 1H), 0.81 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 152.86, 142.58, 131.88, 126.66, 121.80, 41.07, 37.93, 31.68, 31.02, 26.17, 21.05. HRMS (ESI): calcd for $C_{12}H_{15}O_3$ $[M + H]^+$: 207.1021; found 207.1014.


3w

(*R*)-4-(3-methyl-6-(propan-2-ylidene)cyclohex-1-en-1-yl)-1,3-dioxol-2-one (3w): The title compound was prepared according to the condition A. Yellow oil (31.0 mg, 70%; eluent: 2%-10% ethyl acetate/hexane). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.80 (s, 1H), 6.01 (d, *J* = 3.7 Hz, 1H), 2.45 – 2.35 (m, 2H), 2.24 – 2.15 (m, 1H), 1.92 (dtd, *J* = 10.6, 6.3, 4.4 Hz, 1H), 1.76 (s, 3H), 1.67 (s, 3H), 1.36 – 1.28 (m, 1H), 1.07 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 153.00, 144.72, 138.85, 129.13, 125.83, 124.96, 124.47, 31.92, 31.38, 27.19, 23.47, 21.51, 20.98. HRMS (ESI): calcd for $C_{13}H_{17}O_3$ $[M + H]^+$: 221.1178; found 221.1173.

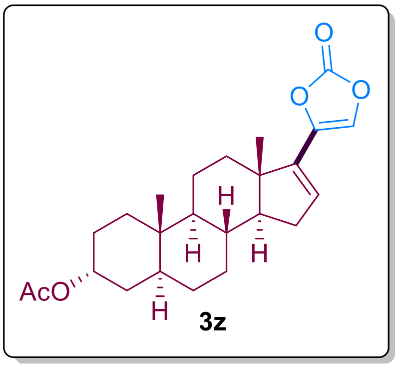

3x

(3*S*,3a*S*,5a*S*,9b*S*)-3,5a,9-trimethyl-8-(2-oxo-1,3-dioxol-4-yl)-3a,4,5,5a,6,9b-hexahydronaphtho[1,2-*b*]furan-2(3*H*)-one (3x): The title compound was prepared according to the condition B. Light yellow solid (35.9 mg, 57%; eluent: 5%-20% ethyl acetate/hexane). **m.p.** = 183-184 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.92 (s, 1H), 6.20 (dd, *J* = 6.1, 3.8 Hz, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 2.24 (dq, *J* = 13.8, 6.9 Hz, 1H), 2.13 (t, *J* = 5.1 Hz, 2H), 1.99 (d, *J* = 2.0 Hz, 3H), 1.91 – 1.85 (m, 1H), 1.84 – 1.71 (m, 2H), 1.51 – 1.33 (m, 2H), 1.20 (d, *J* = 6.9 Hz, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.42, 152.61, 143.18, 134.76, 129.21, 126.33, 125.84, 122.31, 82.22, 51.53, 42.06, 40.92, 40.31, 36.60, 24.26, 22.88, 16.13, 12.41. HRMS (ESI): calcd for $C_{18}H_{21}O_5$ $[M + H]^+$: 317.1389; found 317.1388.


3y

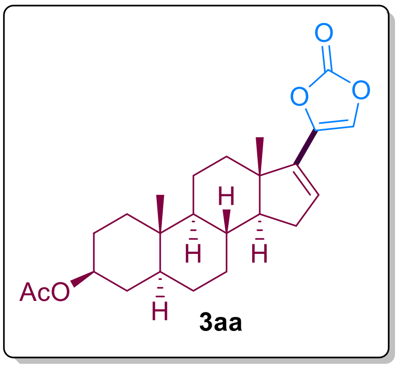
4-((8*S*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)-1,3-dioxol-2-one (3y): The title compound was prepared according to the condition B. Light yellow solid (45.7 mg, 65%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 133-134 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (d, *J* = 8.6 Hz, 1H), 7.00 (s, 1H), 6.72 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.65 (d, *J* = 2.6 Hz, 1H), 6.21 – 6.16 (m, 1H), 3.78 (s, 3H), 2.99 – 2.82 (m, 2H), 2.41 (ddd, *J* = 16.3, 6.3, 3.5 Hz, 2H), 2.31 (td, *J* = 11.0, 4.6 Hz, 1H), 2.12 (dd, *J* = 16.3, 11.5 Hz, 1H), 1.98 – 1.89 (m, 2H), 1.74 (ddd, *J* =

17.6, 9.0, 4.3 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.46 (ddd, *J* = 23.8, 11.6, 7.0 Hz, 1H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.63, 152.56, 140.85, 138.52, 137.80, 132.21, 131.04, 125.98, 124.22, 113.92, 111.57, 56.03, 55.23, 46.68, 44.06, 36.94, 35.04, 31.66, 29.61, 27.64, 26.44, 16.50. HRMS (ESI): calcd for $C_{22}H_{25}O_4$ $[M + H]^+$: 353.1753; found 353.1742.



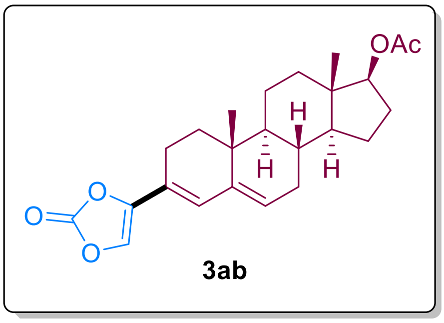
3z

(3*R*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-(2-oxo-1,3-dioxol-4-yl)-2,3,4,5,6,7,8,9,10,11,12,13,14,15-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (3z): The title compound was prepared according to the condition B. White solid (55.9 mg, 70%; eluent: 2%-20% ethyl acetate/hexane). **m.p.** = 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.14 (s, 1H), 5.02 (s, 1H), 2.30 (ddd, *J* = 16.5, 6.3, 3.4 Hz, 1H), 2.05 (s, 3H), 2.00 (dd, *J* = 13.1, 8.4 Hz, 1H), 1.82 (dd, *J* = 9.2, 6.8 Hz, 1H), 1.76 – 1.60 (m, 5H), 1.59 – 1.44 (m, 7H), 1.40 (dd, *J* = 12.9, 4.1 Hz, 1H), 1.30 – 1.21 (m, 3H), 1.10 – 0.97 (m, 1H), 0.92 (s, 3H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.70, 152.57, 140.87, 138.40, 131.10, 124.13, 69.95, 56.79, 54.40, 46.44, 40.12, 35.97, 35.02, 33.61, 32.82, 32.66, 31.82, 31.61, 28.13, 26.04, 21.56, 20.64, 16.45, 11.31. HRMS (ESI): calcd for $C_{24}H_{33}O_5$ $[M + H]^+$: 401.2328; found 401.2317.



3aa

(3*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-(2-oxo-1,3-dioxol-4-yl)-2,3,4,5,6,7,8,9,10,11,12,13,14,15-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (3aa): The title compound was prepared according to the condition B. White solid (48.4 mg, 60%; eluent: 2%-20% ethyl acetate/hexane). **m.p.** = 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.16 – 6.10 (m, 1H), 4.75 – 4.63 (m, 1H), 2.29 (ddd, *J* = 16.5, 6.4, 3.5 Hz, 1H), 2.02 (s, 3H), 2.01 – 1.95 (m, 1H), 1.83 – 1.80 (m, 1H), 1.75 – 1.58 (m, 5H), 1.57 – 1.30 (m, 7H), 1.29 – 1.15 (m, 2H), 1.08 – 0.95 (m, 2H), 0.91 (s, 3H), 0.86 (s, 3H), 0.78 (ddd, *J* = 11.4, 10.3, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.65, 152.54, 140.86, 138.39, 131.10, 124.11, 73.50, 56.65, 54.45, 46.45, 44.78, 36.52, 35.66, 34.99, 33.95, 33.65, 31.83, 31.65, 28.34, 27.40, 21.43, 21.03, 16.44, 12.17. HRMS (ESI): calcd for $C_{24}H_{32}NaO_5$ $[M + Na]^+$: 423.2147; found 423.2138.

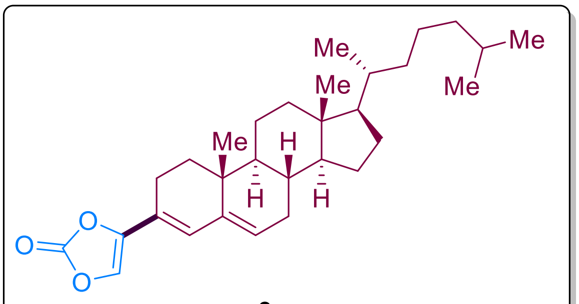


3ab

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-(2-oxo-1,3-dioxol-4-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acetate (3ab): The title compound was prepared according to the condition B. Yellow solid (45.9 mg, 58%; eluent: 2%-20% ethyl -acetate/hexane). **m.p.** = 164-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.38 (s, 1H), 5.70 – 5.66 (m, 1H), 4.62 (dd, *J* = 8.9, 8.1 Hz, 1H), 2.33 – 2.17 (m, 3H), 2.15 – 2.10 (m, 1H), 2.05 (s, 3H), 1.95 – 1.88 (m, 1H), 1.84 – 1.75 (m, 2H), 1.70

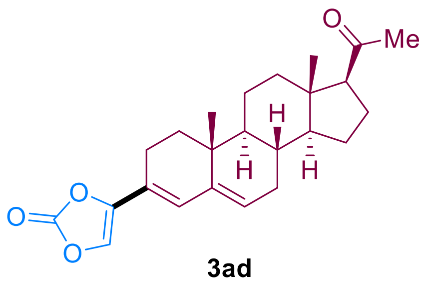
– 1.60 (m, 2H), 1.59 – 1.31 (m, 4H), 1.25 (td, *J* = 12.3, 4.9 Hz, 2H), 1.15 – 1.04 (m, 2H), 0.97 (s, 3H), 0.84 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 171.19, 152.69, 144.37, 140.37, 128.76, 127.82, 124.24, 117.54, 82.61, 51.18, 48.02, 42.53, 36.68, 35.01, 32.77, 31.67, 31.48, 27.50, 23.45, 21.16, 20.58, 20.54, 19.13, 12.04. HRMS (ESI): calcd for $C_{24}H_{31}O_5$ $[M + H]^+$: 399.2171; found 399.2160.

4-((8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)-1,3-dioxol-2-one (3ac): The title compound was prepared according to the condition B. Yellow solid (47.9 mg, 53%; eluent: 2%-5% ethyl acetate/hexane). **m.p.** = 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.30 (s, 1H), 5.61 (s, 1H), 2.18 (dt, *J* = 18.6, 4.8 Hz, 2H), 2.05 – 1.93 (m, 2H), 1.88 – 1.74 (m, 2H), 1.72 – 0.93 (m, 20H), 0.88 (s, 3H), 0.85 (d, *J* = 6.5 Hz, 3H), 0.80 (d, *J* = 1.5 Hz, 3H), 0.79 (d, *J* = 1.5 Hz, 3H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.74, 144.46, 140.33, 129.42, 128.00, 124.12, 117.35, 56.82, 56.17, 48.06, 42.46, 39.69, 39.52, 36.20, 35.82, 34.97, 32.78, 32.18, 31.65, 28.23, 28.03, 24.16, 23.89, 22.84, 22.59, 21.05, 20.62, 19.13, 18.73, 11.99. HRMS (ESI): calcd for $C_{30}H_{45}O_3$ $[M + H]^+$: 453.3369; found 453.3357.



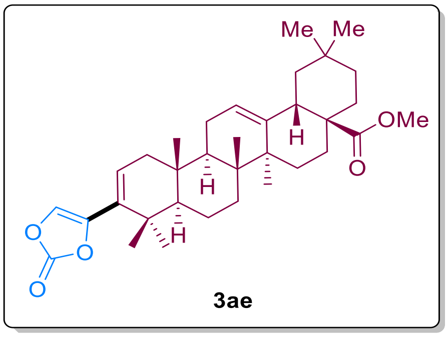
3ac

4-((8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)-1,3-dioxol-2-one (3ad): The title compound was prepared according to the condition B. Light yellow solid (58.2 mg, 76%; eluent: 2%-20% ethyl acetate/hexane). **m.p.** = 180-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.37 (s, 1H), 5.68 (d, *J* = 4.0 Hz, 1H), 2.56 (t, *J* = 8.9 Hz, 1H), 2.35 – 2.17 (m, 4H), 2.14 (s, 3H), 2.11 – 2.06 (m, 1H), 1.93 (dd, *J* = 12.7, 4.2 Hz, 1H), 1.73 – 1.64 (m, 4H), 1.54 – 1.42 (m, 2H), 1.33 – 1.18 (m, 4H), 1.14 – 1.04 (m, 1H), 0.96 (s, 3H), 0.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.41, 152.67, 144.33, 140.27, 128.87, 127.75, 124.31, 117.54, 63.55, 56.89, 47.89, 44.02, 38.67, 34.96, 32.75, 31.98, 31.60, 31.53, 24.34, 22.82, 21.01, 20.56, 19.10, 13.32. HRMS (ESI): calcd for $C_{24}H_{31}O_4$ $[M + H]^+$: 383.2222; found 383.2216.



3ad

Methyl (4a*S*,6a*S*,6b*R*,8a*R*,12a*S*,12b*R*,14b*S*)-2,2,6a,6b,9,9,12a-heptamethyl-10-(2-oxo-1,3-dioxol-4-yl)-1,3,4,5,6,6a,6b,7,8,8a,9,12,12a,12b,13,14b-hexadecahydropicene-4a(2*H*)-carboxylate (3ae): The title compound was prepared according to the condition C. White solid (39.6 mg, 37%; eluent: 2%-20% ethyl acetate/hexane). **m.p.** = 199-200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.04 (d, *J* = 4.7 Hz, 1H), 5.26 (s, 1H), 3.56 (s, 3H), 2.81 (dd, *J* = 13.7, 3.6 Hz, 1H), 2.10 (dd, *J* = 18.2, 6.6 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.84 – 1.75 (m, 1H), 1.70 – 1.18 (m, 16H), 1.07 (s, 6H), 0.99 (s, 3H), 0.86 (s, 6H), 0.83 (s, 3H), 0.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.28, 152.69, 144.15, 143.74, 130.87, 128.74, 125.26, 122.24, 53.23, 51.58, 46.81, 46.25, 45.85, 41.80, 41.46, 41.29, 39.24, 35.74, 35.59, 33.88, 33.12, 32.35, 32.10, 30.72, 29.75, 27.65, 25.73, 23.62, 23.21, 23.10, 21.05, 19.44, 16.52, 15.72. HRMS (ESI): calcd for $C_{34}H_{49}O_5$ [M + H]$^+$: 537.3580; found 537.3579.



3ae

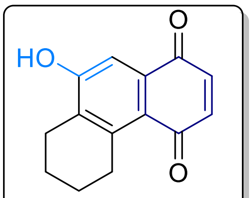
V. Tandem Diels-Alder cycloaddition/decarboxylative aromatization reactions enabled concise syntheses of substituted 2-naphthols

Step 1

Condition A: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **3** (0.2 mmol), benzoquinone (0.8 mmol, 86.4 mg) and acetic acid (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at pre-heated 80 °C heating mantle for 48 h. Up completion, saturated aqueous sodium bicarbonate solution was added to neutralize the acid. The aqueous mixture was extracted with ethyl acetate (25 mL) for three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, and the filtrate was concentrated under reduced pressure. The residue was then purified by silica gel chromatography to obtain the corresponding product **5**.

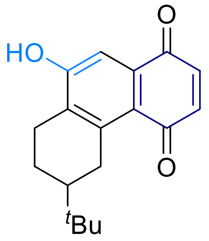
Condition B: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **3** (0.2 mmol), benzoquinone (0.8 mmol, 86.4 mg) and *tert*-butanol (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at pre-heated 80 °C heating mantle for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **5**.

9-Hydroxy-5,6,7,8-tetrahydrophenanthrene-1,4-dione (5a): The title compound was prepared according to the condition A. Yellow solid (41.2 mg, 90%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 235-236 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.85 (s, 1H), 7.27 (s, 1H), 6.83 (q, J = 10.2 Hz, 2H), 3.09 (s, 2H), 2.62 (s, 2H), 1.70 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 186.12, 185.75, 159.94, 143.07, 141.54, 135.99, 132.87, 131.41, 121.64, 109.69, 29.11, 24.39, 22.63, 21.37. HRMS (ESI): calcd for $C_{14}H_{11}O_3$ $[M - H]^-$: 227.0714; found 227.0712.



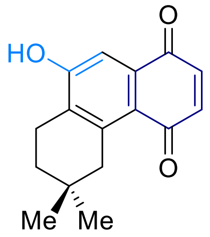
5a

6-(*Tert*-butyl)-9-hydroxy-5,6,7,8-tetrahydrophenanthrene-1,4-dione (5b): The title compound was prepared according to the condition A. Yellow solid (30.1 mg, 53%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 230-231 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.79 (s, 1H), 7.23 (s, 1H), 6.77 (dd, J = 28.7, 10.2 Hz, 2H), 3.36 – 3.28 (m, 1H), 2.87 (dd, J = 17.9, 3.5 Hz, 1H), 2.61 – 2.52 (m, 1H), 2.35 (ddd, J = 17.8, 12.4, 5.5 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.26 – 1.16 (m, 1H), 1.15 – 1.06 (m, 1H), 0.95 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 186.02, 185.64, 159.68, 143.62, 141.44, 135.79, 133.03, 131.22, 121.65, 109.66, 43.89, 32.59, 30.72, 27.48, 25.47, 22.72. HRMS (ESI): calcd for $C_{18}H_{19}O_3$ $[M - H]^-$: 283.1340; found 283.1346.



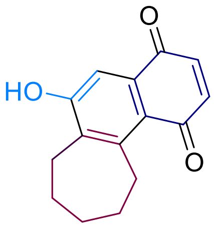
5b

9-Hydroxy-6,6-dimethyl-5,6,7,8-tetrahydrophenanthrene-1,4-dione (5c): The title compound was prepared according to the condition A. Yellow solid (43.8 mg, 86%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 225-226 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.89 (s, 1H), 7.29 (s, 1H), 6.82 (q, J = 10.2 Hz, 2H), 2.90 (s, 2H), 2.63 (t, J = 6.7 Hz, 2H), 1.49 (t, J = 6.8 Hz, 2H), 0.93 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 186.23, 185.75, 159.90, 142.24, 141.60, 136.01, 133.26, 130.14, 121.94, 109.68, 42.43, 33.61, 28.69, 28.48, 21.75. HRMS (ESI): calcd for $C_{16}H_{15}O_3$ $[M - H]^-$: 255.1027; found 255.1027.

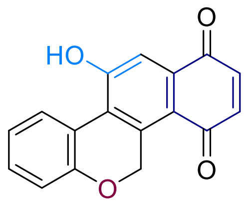


5c

6-Hydroxy-8,9,10,11-tetrahydro-1*H*-cyclohepta[*a*]naphthalene-1,4(7*H*)-dione (5d): The title compound was prepared according to the condition A. Yellow solid (23.3 mg, 48%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 213-214 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.78 (s, 1H), 7.34 (s, 1H), 6.85 (s, 2H), 3.41 – 3.38 (m, 2H), 2.95 – 2.87 (m, 2H), 1.76 (dd, J = 11.4, 5.9 Hz, 2H), 1.58 (d, J = 3.9 Hz, 2H), 1.55 – 1.46 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 186.90, 185.53, 158.54, 149.55, 141.94, 137.82, 136.16, 132.83, 121.89, 111.33, 31.51, 28.51, 26.86, 26.50, 24.70. HRMS (ESI): calcd for $C_{15}H_{13}O_3$ $[M - H]^-$: 241.0871; found 241.0870.

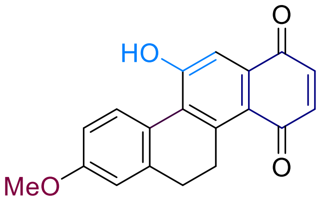


5d



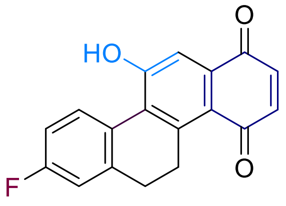
5e

11-Hydroxy-1*H*-naphtho[1,2-*c*]chromene-1,4(5*H*)-dione (5e): The title compound was prepared according to the condition B. Red solid (28.4 mg, 51%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** >300 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.65 (s, 1H), 8.37 (dd, J = 8.0, 1.4 Hz, 1H), 7.50 (s, 1H), 7.30 (td, J = 8.0, 1.5 Hz, 1H), 7.10 – 7.05 (m, 1H), 7.00 (dd, J = 8.0, 0.9 Hz, 1H), 6.94 – 6.87 (m, 2H), 5.46 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 185.89, 184.74, 158.90, 155.03, 141.07, 139.03, 137.11, 133.24, 130.43, 129.32, 122.16, 122.11, 120.92, 120.32, 116.90, 113.68, 65.87. HRMS (ESI): calcd for $C_{17}H_9O_4$ $[M - H]^-$: 277.0507; found 277.0505.



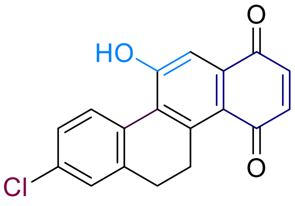
5f

11-Hydroxy-8-methoxy-5,6-dihydrochrysene-1,4-dione (5f): The title compound was prepared according to the condition B. Red solid (22.8 mg, 37%; eluent: 10%-30% ethyl acetate/hexane) **m.p.** = 192-193 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.18 (s, 1H), 8.23 (d, J = 8.7 Hz, 1H), 7.50 (s, 1H), 6.91 – 6.87 (m, 3H), 6.85 (dd, J = 8.7, 2.8 Hz, 1H), 3.80 (s, 3H), 3.31 – 3.24 (m, 2H), 2.70 – 2.62 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 186.40, 185.12, 159.28, 158.47, 144.31, 141.93, 140.74, 136.54, 132.63, 130.72, 127.75, 123.82, 121.97, 113.03, 112.62, 111.97, 55.54, 28.79, 26.24. HRMS (ESI): calcd for $C_{19}H_{13}O_4$ $[M - H]^-$: 305.0819; found 305.0828.



5g

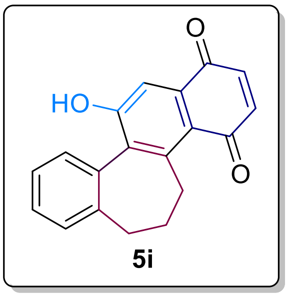
8-Fluoro-11-hydroxy-5,6-dihydrochrysene-1,4-dione (5g): The title compound was prepared according to the condition B. Red solid (28.2 mg, 48%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 239-240 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.23 (s, 1H), 8.20 (dd, J = 8.0, 6.5 Hz, 1H), 7.38 (s, 1H), 7.02 (dd, J = 18.1, 9.0 Hz, 2H), 6.80 – 6.70 (m, 2H), 3.22 – 3.08 (m, 2H), 2.59 (d, J = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 186.09, 184.97, 161.68 (d, J = 246.2 Hz), 158.75, 144.69, 141.87, 141.79, 136.39, 133.21, 131.33 (d, J = 8.3 Hz), 127.56 (d, J = 2.9 Hz), 126.65, 121.76, 113.98 (d, J = 21.2 Hz), 113.09, 112.90, 28.35, 25.92. ^{19}F NMR (377 MHz, DMSO) δ -113.44. HRMS (ESI): calcd for $C_{18}H_{10}FO_3$ $[M - H]^-$: 293.0620; found 293.0618.



5h

8-Chloro-11-hydroxy-5,6-dihydrochrysene-1,4-dione (5h): The title compound was prepared according to the condition B. Red solid (22.9 mg, 37%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 228-229 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.32 (s, 1H), 8.19 (d, J = 8.6 Hz, 1H), 7.42 (s, 1H), 7.30 (d, J = 2.0 Hz, 1H), 7.25 (dd, J = 8.6, 2.2 Hz, 1H), 6.84 – 6.77 (m, 2H), 3.24 – 3.17 (m, 2H), 2.64 – 2.57 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 185.96, 184.89, 158.99, 144.98, 141.83, 141.08, 136.33, 133.45, 132.50, 130.80, 129.99, 126.96, 126.34, 126.20, 121.67, 113.11, 28.06, 25.89. HRMS (ESI): calcd for $C_{18}H_{10}ClO_3$ $[M - H]^-$: 309.0325; found 309.0323.

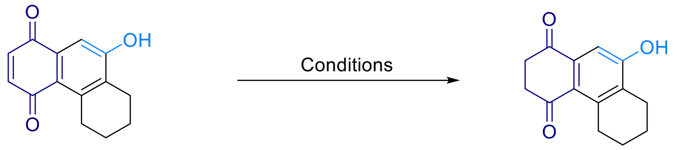
9-Hydroxy-2,3-dihydro-1*H*-benzo[3,4]cyclohepta[1,2-*a*]naphthalene-10,13-dione (5i): The title compound was prepared according to the condition B. Red solid (25.4 mg, 44%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 177-178 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.93 (s, 1H), 7.53 – 7.48 (m, 2H), 7.33 – 7.26 (m, 3H), 6.92 – 6.86 (m, 2H), 3.80 (dd, *J* = 11.6, 3.3 Hz, 1H), 2.55 (dd, *J* = 11.8, 6.1 Hz, 1H), 2.22 – 2.10 (m, 2H), 2.04 – 1.94 (m, 1H), 1.80 (td, *J* = 12.3, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 186.45, 185.27, 158.24, 144.79, 141.84, 140.12, 136.46, 134.72, 134.02, 133.43, 130.81, 128.58, 128.46, 125.97, 121.90, 112.53, 32.09, 31.09, 27.25. HRMS (ESI): calcd for $C_{19}H_{13}O_3$ [M - H]$^-$: 289.0871; found 289.0870.



5i

Step 2

Table S4. Optimization of the reduction conditions



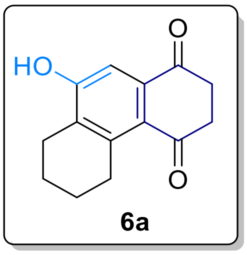
5a

6a

Entry	Reaction conditions	Isolated yield of **6a**
1	5 equiv $NaBH_4$/MeOH/rt/24h	Complex mixture
2	5 equiv $NaBH_4$/MeOH/reflux/24h	Complex mixture
3	1 equiv $CeCl_3 \cdot H_2O$/4 equiv $NaBH_4$/MeOH/rt/24h	Complex mixture
4	10 mol% PtO_2/H_2/EtOH/rt/0.5h	NR
5	20 equiv $SnCl_2$/4N HCl (7 mL)/reflux/75 min	trace
6	3 equiv $SnCl_2$/TFA/100 °C/1.5h	37%
7	3 equiv $SnCl_2$/HOAc/100 °C/1.5h	82%

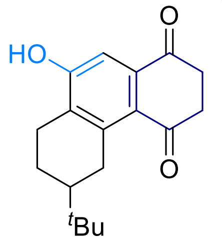
Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **5** (0.2 mmol), $SnCl_2$ (0.6 mmol, 114 mg) and acetic acid (4 mL) under Air. The reaction mixture was stirred at pre-heated 100 °C heating mantle for 1.5 h. Upon completion, saturated aqueous sodium bicarbonate solution was added to neutralize the acid. The aqueous mixture was extracted with ethyl acetate (25 mL) for three times. The combined organic layer was dried over anhydrous sodium sulfate, filtered, and the filtrate was concentrated under reduced pressure. The residue was then purified by silica gel chromatography to obtain the corresponding product **6**.

9-Hydroxy-2,3,5,6,7,8-hexahydrophenanthrene-1,4-dione (6a): The title compound was prepared according to the abovementioned procedure. Yellow solid (37.8 mg, 82%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 253-254 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.68 (s, 1H), 7.23 (s, 1H), 3.03 (d, *J* = 5.6 Hz, 2H), 2.98 – 2.86 (m, 4H), 2.60 (d, *J* = 5.8 Hz, 2H), 1.70 – 1.64 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 197.61, 196.89, 159.64, 141.58, 136.09, 131.94, 126.14, 108.73, 37.62, 28.98, 24.47, 22.78, 21.48.



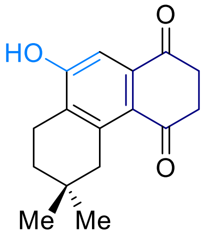
6a

HRMS (ESI): calcd for $C_{14}H_{13}O_3$ [M - H]$^-$: 229.0871; found 229.0869.



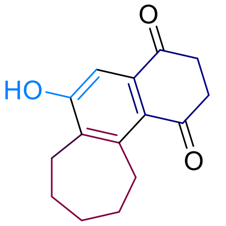
6b

6-(*Tert*-butyl)-9-hydroxy-2,3,5,6,7,8-hexahydrophenanthrene-1,4-dione (6b): The title compound was prepared according to the abovementioned procedure. Gray solid (34 mg, 59%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 204-205 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.62 (s, 1H), 7.19 (s, 1H), 3.31 – 3.19 (m, 1H), 2.99 – 2.82 (m, 4H), 2.81 – 2.73 (m, 1H), 2.60 – 2.52 (m, 1H), 2.35 (ddd, *J* = 17.8, 12.2, 5.6 Hz, 1H), 1.91 (dd, *J* = 11.6, 4.1 Hz, 1H), 1.17 (td, *J* = 12.3, 3.4 Hz, 1H), 1.12 – 1.03 (m, 1H), 0.90 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 197.54, 196.81, 159.44, 142.16, 136.31, 131.82, 126.16, 108.70, 44.13, 39.54, 37.60, 32.59, 30.56, 27.50, 25.59, 22.85. HRMS (ESI): calcd for $C_{18}H_{21}O_3$ [M - H]$^-$: 285.1497; found 285.1497.



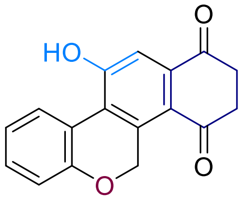
6c

9-Hydroxy-6,6-dimethyl-2,3,5,6,7,8-hexahydrophenanthrene-1,4-dione (6c): The title compound was prepared according to the abovementioned procedure. Yellow solid (39 mg, 76%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 195-196 °C.^{1}H NMR (400 MHz, DMSO) δ 10.72 (s, 1H), 7.25 (s, 1H), 2.98 – 2.87 (m, 4H), 2.85 (s, 2H), 2.64 (t, *J* = 6.7 Hz, 2H), 1.49 (t, *J* = 6.8 Hz, 2H), 0.91 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 197.77, 196.83, 159.57, 140.67, 136.50, 130.70, 126.47, 108.71, 42.35, 39.60, 37.65, 33.74, 28.79, 28.41, 21.89. HRMS (ESI): calcd for $C_{16}H_{17}O_3$ [M - H]$^-$: 257.1184; found 257.1180.



6d

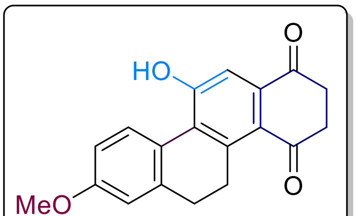
6-Hydroxy-2,3,8,9,10,11-hexahydro-1*H*-cyclohepta[*a*]naphthalene-1,4(7*H*)-dione (6d): The title compound was prepared according to the abovementioned procedure. Yellow solid (35.6 mg, 73%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 223-224 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.58 (s, 1H), 7.28 (s, 1H), 3.23 – 3.19 (m, 2H), 3.00 – 2.89 (m, 6H), 1.76 (dd, *J* = 11.3, 5.8 Hz, 2H), 1.57 (d, *J* = 4.0 Hz, 2H), 1.51 (d, *J* = 4.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 198.86, 196.43, 158.08, 147.57, 138.36, 135.81, 127.01, 110.34, 37.84, 31.67, 28.99, 26.89, 26.82, 24.95. HRMS (ESI): calcd for $C_{15}H_{15}O_3$ [M - H]$^-$: 243.1027; found 243.1026.



6e

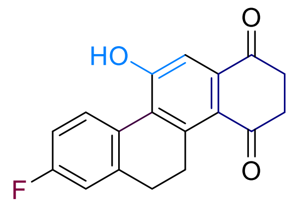
11-Hydroxy-2,3-dihydro-1*H*-naphtho[1,2-*c*]chromene-1,4(5*H*)-dione (6e): The title compound was prepared according to the abovementioned procedure. Red solid (27.8 mg, 50%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** > 300 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.54 (s, 1H), 8.40 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.50 (s, 1H), 7.34 – 7.28 (m, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.39 (s, 2H), 3.02 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 197.60, 196.02, 158.69, 155.48, 137.88, 136.67, 130.45, 129.34, 124.85, 122.65, 122.18, 121.17, 116.93, 112.89, 65.99, 38.68, 37.49. HRMS (ESI): calcd for $C_{17}H_{11}O_4$ [M - H]$^-$: 279.0664; found 279.0661.

11-Hydroxy-8-methoxy-2,3,5,6-tetrahydrochrysene-1,4-dione (6f): The title compound was prepared according to the abovementioned procedure. Red solid (34.2 mg, 56%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 173-174 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.02 (s, 1H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.46 (s, 1H), 6.85 (dt, *J* = 8.7, 2.6 Hz, 2H), 3.79 (s, 3H), 3.17 – 3.08 (m, 2H), 2.98 (d, *J* = 2.8 Hz, 4H), 2.66 – 2.58 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 198.02, 196.18, 159.24, 158.21, 142.41, 141.03, 135.74, 130.69, 128.17, 126.48, 124.04, 112.65, 112.08, 111.88, 55.50, 39.67, 37.70, 29.01, 26.20. HRMS (ESI): calcd for $C_{19}H_{15}O_4$ [M - H]$^-$: 307.0977; found 307.0975.



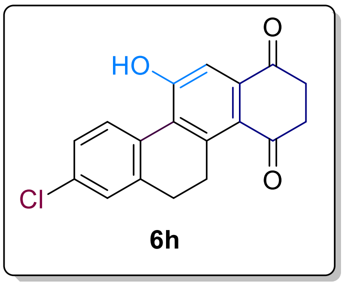
6f

8-Fluoro-11-hydroxy-2,3,5,6-tetrahydrochrysene-1,4-dione (6g): The title compound was prepared according to the abovementioned procedure. Red solid (40.5 mg, 69%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 244-245 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.17 (s, 1H), 8.30 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.47 (s, 1H), 7.16 – 7.04 (m, 2H), 3.17 – 3.10 (m, 2H), 3.04 – 2.92 (m, 4H), 2.69 – 2.60 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 197.83, 196.17, 161.71 (d, *J* = 246.2 Hz), 158.49, 142.99, 142.17 (d, *J* = 8.0 Hz), 136.42, 131.29 (d, *J* = 8.2 Hz), 127.79 (d, *J* = 2.9 Hz), 127.13, 126.38, 114.03 (d, *J* = 21.2 Hz), 113.00 (d, *J* = 20.7 Hz), 112.19, 39.57, 37.68, 28.61, 25.98. ^{19}F NMR (377 MHz, DMSO) δ -113.51. HRMS (ESI): calcd for $C_{18}H_{12}FO_3$ [M - H]$^-$: 295.0777; found 295.0776.



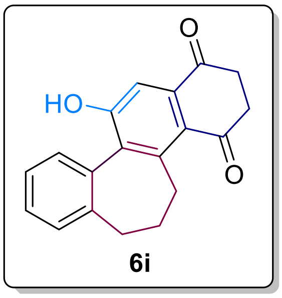
6g

8-Chloro-11-hydroxy-5,6-dihydrochrysene-1,4-dione (6h): The title compound was prepared according to the abovementioned procedure. Yellow solid (46.7 mg, 75%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 225-226 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.26 (s, 1H), 8.28 (d, *J* = 8.6 Hz, 1H), 7.47 (s, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.33 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.18 – 3.13 (m, 2H), 3.04 – 2.96 (m, 4H), 2.70 – 2.62 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 197.82, 196.21, 158.75, 143.37, 141.53, 136.75, 132.53, 130.80, 130.27, 127.12, 126.86, 126.39, 126.29, 112.20, 37.70, 28.32, 26.02. HRMS (ESI): calcd for $C_{18}H_{12}ClO_3$ [M - H]$^-$: 311.0481; found 311.0479.



6h

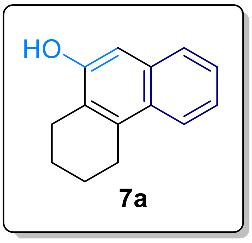
8-Chloro-11-hydroxy-5,6-dihydrochrysene-1,4-dione (6i): The title compound was prepared according to the abovementioned procedure. Yellow solid (43.8 mg, 75%; eluent: 10%-30% ethyl acetate/hexane). **m.p.** = 191-192 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.75 (s, 1H), 7.53 – 7.50 (m, 1H), 7.49 (s, 1H), 7.33 – 7.31 (m, 1H), 7.31 – 7.28 (m, 2H), 3.58 – 3.51 (m, 1H), 3.20 – 3.02 (m, 2H), 3.01 – 2.93 (m, 1H), 2.87 – 2.79 (m, 1H), 2.57 (dd, J = 12.2, 5.9 Hz, 1H), 2.27 – 2.11 (m, 2H), 2.07 – 1.97 (m, 1H), 1.79 (td, J = 12.4, 6.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 198.28, 196.39, 157.87, 143.20, 140.13, 137.21, 135.01, 133.91, 130.77, 128.53, 128.45, 126.88, 125.95, 111.64, 39.67, 37.78, 32.78, 30.99, 27.56. HRMS (ESI): calcd for $C_{19}H_{15}O_3$ [M - H]$^-$: 291.1027; found 291.1026.



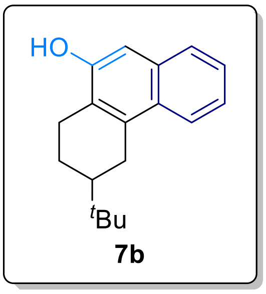
Step 3

Procedure: An oven dried 25 mL round bottom flask equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the flask was charged with **6** (0.2 mmol) and THF (10 mL), and was evacuated and refilled with Argon for three times. Then, $LiAlH_4$ (0.6 mmol, 1M THF, 0.6 mL) was dropwise added to the reaction mixture, which was stirred at room temperature for 1.5 h. Upon completion, 2M HCl was added to adjust the pH of the mixture to be slight acidic. The aqueous phase was extracted with ethyl acetate (25 mL) for three times, and the combined organic layer was dried over anhydrous sodium sulfate, filtered and the filtrate was concentrated under reduced pressure. The residue was then purified by silica gel chromatography to obtain the corresponding product **7**.

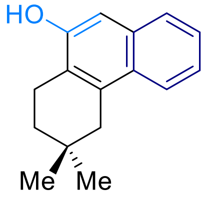
5,6,7,8-Tetrahydrophenanthren-9-ol (7a): The title compound was prepared according to the abovementioned procedure. White solid (23.5 mg, 60%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 112-113 °C. ^{1}H NMR (400 MHz, DMSO) δ 9.68 (s, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.25 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 7.01 (s, 1H), 2.99 (t, J = 6.0 Hz, 2H), 2.71 (t, J = 6.0 Hz, 2H), 1.88 – 1.72 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 154.17, 133.25, 133.21, 127.28, 126.99, 126.63, 125.37, 123.00, 122.91, 106.29, 25.86, 24.30, 22.90, 22.55. HRMS (ESI): calcd for $C_{14}H_{13}O$ [M - H]$^-$: 197.0973; found 197.0972.



6-(*Tert*-butyl)-5,6,7,8-tetrahydrophenanthren-9-ol (7b): The title compound was prepared according to the abovementioned procedure. Yellow oil (38.1 mg, 75%; eluent: 2%-10% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 9.66 (s, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.0 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.98 (s, 1H), 3.17 (dd, J = 16.8, 4.4 Hz, 1H), 3.00 (dd, J = 17.6, 3.6 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.48 (dd, J = 22.2, 3.0 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.45 (ddd, J = 11.9, 4.7, 3.2 Hz, 1H), 1.28 – 1.15 (m, 1H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 154.01, 133.54, 133.37, 127.46, 126.97, 126.67, 125.35, 123.04, 122.90, 106.21, 44.27, 32.77, 27.63, 25.64, 23.96. HRMS (ESI): calcd for $C_{18}H_{21}O$ [M - H]$^-$: 253.1599; found 253.1598.

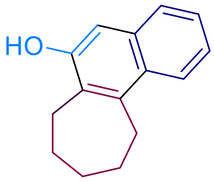


6,6-Dimethyl-5,6,7,8-tetrahydrophenanthren-9-ol (7c): The title compound was prepared according to the abovementioned procedure. White solid (29.9 mg, 66%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 98-99 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.72 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.03 (s, 1H), 2.79 (s, 2H), 2.75 (t, *J* = 6.5 Hz, 2H), 1.56 (t, *J* = 6.6 Hz, 2H), 1.01 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 154.14, 133.52, 132.48, 127.44, 126.69, 125.57, 125.34, 122.97, 122.86, 106.28, 39.55, 34.96, 29.05, 28.61, 21.89.HRMS (ESI): calcd for $C_{16}H_{17}O$ [M - H]$^{-}$: 225.1286; found 225.1286.



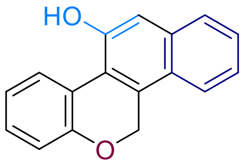
7c

8,9,10,11-Tetrahydro-7*H*-cyclohepta[*a*]naphthalen-6-ol (7d): The title compound was prepared according to the abovementioned procedure. White solid (37.3 mg, 88%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 127-128 ºC. ^{1}H NMR (400 MHz, DMSO) δ 9.70 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.08 (s, 1H), 3.21 – 3.15 (m, 2H), 3.06 – 3.01 (m, 2H), 1.83 (s, 2H), 1.62 – 1.49 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 153.27, 140.95, 133.84, 132.58, 126.85, 126.52, 125.28, 123.72, 122.95, 107.46, 32.31, 27.88, 27.06, 27.02, 25.52. HRMS (ESI): calcd for $C_{15}H_{15}O$ [M - H]$^{-}$: 211.1129; found 211.1128.



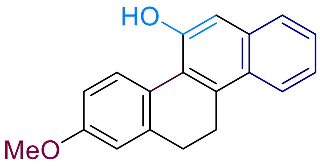
7d

5*H*-naphtho[1,2-*c*]chromen-11-ol (7e): The title compound was prepared according to the abovementioned procedure. Light yellow solid (25.6 mg, 52%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 163-165 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.45 (s, 1H), 8.54 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.29 (s, 1H), 7.29 – 7.24 (m, 1H), 7.11 – 7.07 (m, 1H), 7.07 – 7.03 (m, 1H), 5.53 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 155.05, 153.01, 134.24, 130.45, 129.30, 129.17, 126.83, 126.77, 124.01, 123.82, 123.45, 122.68, 121.99, 119.16, 116.80, 110.47, 65.10. HRMS (ESI): calcd for $C_{17}H_{11}O_2$ [M - H]$^{-}$: 247.0765; found 247.0765.



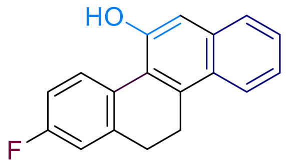
7e

2-Methoxy-11,12-dihydrochrysen-5-ol (7f): The title compound was prepared according to the abovementioned procedure. Red solid (25.7 mg, 47%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 107-108 ºC. ^{1}H NMR (400 MHz, DMSO) δ 10.05 (s, 1H), 8.36 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.20 (s, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.80 (s, 3H), 3.13 – 3.06 (m, 2H), 2.82 – 2.76 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 158.44, 153.33, 139.98, 135.54, 133.75, 130.25, 126.59, 126.42, 126.07, 124.09, 123.93, 123.41, 112.96, 111.71, 109.19, 55.47, 29.51, 24.70. HRMS (ESI): calcd for $C_{19}H_{15}O_2$ [M - H]$^{-}$: 275.1078; found 275.1077.



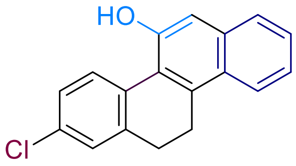
7f

2-Fluoro-11,12-dihydrochrysen-5-ol (7g): The title compound was prepared according to the abovementioned procedure. White solid (23.8 mg, 45%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 145-146 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.21 (s, 1H), 8.46 (dd, *J* = 8.8, 6.1 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.32 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.25 (s, 1H), 7.21 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.12 (td, *J* = 8.9, 2.9 Hz, 1H), 3.18 – 3.13 (m, 2H), 2.88 – 2.83 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 162.36, 159.93, 153.24, 141.17 (d, *J* = 7.8 Hz), 136.43, 134.12, 130.81 (d, *J* = 8.0 Hz), 129.76 (d, *J* = 3.0 Hz), 126.59 (d, *J* = 12.8 Hz), 126.28, 124.32, 123.56, 123.11, 114.18 (d, *J* = 21.1 Hz), 112.85 (d, *J* = 20.4 Hz), 109.33, 29.06, 24.47. ^{19}F NMR (377 MHz, DMSO) δ -115.32. HRMS (ESI): calcd for $C_{18}H_{12}FO$ [M - H]$^{-}$: 263.0878; found 263.0877.



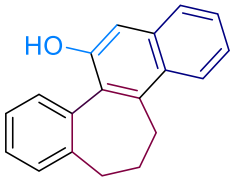
7g

2-Chloro-11,12-dihydrochrysen-5-ol (7h): The title compound was prepared according to the abovementioned procedure. Light yellow solid (24.3 mg, 43%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 125-126 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.24 (s, 1H), 8.42 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.4, 6.0 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.25 (s, 1H), 3.15 – 3.07 (m, 2H), 2.85 – 2.77 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 153.35, 140.61, 136.95, 134.35, 132.24, 131.36, 130.51, 127.20, 126.72, 126.68, 126.25, 126.22, 124.39, 123.61, 122.90, 109.40, 28.76, 24.49. HRMS (ESI): calcd for $C_{18}H_{12}ClO$ [M - H]$^{-}$: 279.0583; found 279.0581.



7h

2,3-Dihydro-1*H*-benzo[3,4]cyclohepta[1,2-*a*]naphthalen-8-ol (7i): The title compound was prepared according to the abovementioned procedure. Light yellow solid (39.0 mg, 75%; eluent: 2%-10% ethyl acetate/hexane). **m.p.** = 125-126 °C. ^{1}H NMR (400 MHz, DMSO) δ 9.76 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.29 (dd, *J* = 5.1, 3.4 Hz, 3H), 7.23 (s, 1H), 3.34 (d, *J* = 16.0 Hz, 1H), 2.54 (t, *J* = 7.1 Hz, 1H), 2.23 – 2.11 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 152.48, 139.99, 137.12, 137.03, 134.71, 131.03, 128.63, 128.48, 127.66, 126.94, 126.26, 126.17, 125.75, 124.28, 123.50, 108.60, 33.45, 31.32, 25.47. HRMS (ESI): calcd for $C_{19}H_{15}O$ [M - H]$^{-}$: 259.1129; found 259.1129.



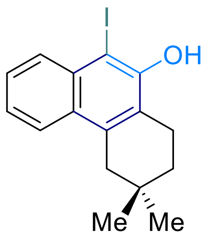
7i

VI. Halogenation of 2-naphthols

Condition A: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **7** (0.1 mmol), TsOH (0.1 mmol, 17.2 mg), NIS (0.1 mmol, 22.4 mg) and MeCN (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at room temperature for 1 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **9**.

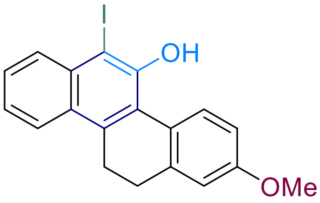
Condition B: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **7** (0.1 mmol), NBS (0.1 mmol, 18.0 mg) and DCM (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at room temperature for 1 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **9**.

10-Iodo-6,6-dimethyl-5,6,7,8-tetrahydrophenanthren-9-ol (9a): The title compound was prepared according to the condition A. Light yellow oil (41.7 mg, 60%; eluent: 0%-2% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 9.19 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.40 – 7.32 (m, 1H), 2.80 (d, *J* = 10.6 Hz, 4H), 1.56 (t, *J* = 6.5 Hz, 2H), 1.00 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 154.02, 133.83, 133.37, 131.30, 129.20, 127.25, 126.39, 124.31, 123.60, 85.56, 39.66, 34.85, 28.91, 28.45, 23.26. HRMS (ESI): calcd for $C_{16}H_{16}IO$ [M - H]$^-$: 351.0252; found 351.0251.



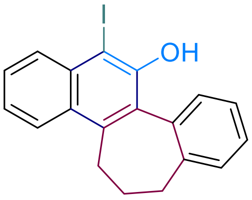
9a

6-Iodo-2-methoxy-11,12-dihydrochrysen-5-ol (9b): The title compound was prepared according to the condition A. Light yellow oil (39.0 mg, 49%; eluent: 0%-3% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 9.43 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 8.03 (dd, *J* = 14.7, 8.2 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.43 – 7.36 (m, 1H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.81 (d, *J* = 3.8 Hz, 2H), 3.15 – 3.06 (m, 1H), 2.85 – 2.77 (m, 1H). ^{13}C NMR (101 MHz, DMSO) δ 158.87, 152.49, 140.19, 136.40, 134.23, 131.69, 129.77, 128.39, 128.00, 126.19, 125.77, 124.87, 124.57, 113.19, 111.94, 90.52, 55.58, 29.22, 25.06. HRMS (ESI): calcd for $C_{19}H_{14}IO_2$ [M - H]$^-$: 401.0045; found 401.0053.



9b

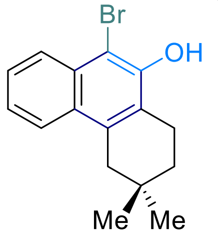
9-Iodo-2,3-dihydro-1*H*-benzo[3,4]cyclohepta[1,2-*a*]naphthalen-8-ol (9c): The title compound was prepared according to the condition A. Light yellow oil (59.8 mg, 78%; eluent: 0%-3% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 9.00 (s, 1H), 8.13 – 8.05 (m, 2H), 7.60 – 7.50 (m, 2H), 7.45 – 7.39 (m, 1H), 7.38 – 7.34 (m, 1H), 7.32 (t, *J* = 4.5 Hz, 2H), 3.45 – 3.33 (m, 1H), 2.57 (d, *J* = 11.2 Hz, 1H), 2.22 (dd, *J* = 19.7, 11.3 Hz, 1H), 2.16 – 2.06 (m, 3H). ^{13}C NMR (101 MHz, DMSO) δ 152.29, 140.38, 137.63, 136.77, 135.12, 131.78, 130.56, 129.78,



9c

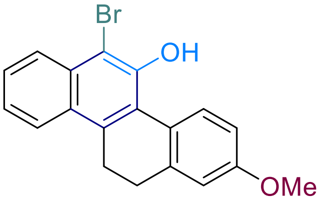
128.65, 128.34, 128.22, 127.90, 126.29, 125.03, 124.89, 88.75, 33.14, 31.15, 25.65. HRMS (ESI): calcd for $C_{19}H_{14}IO$ [M - H]$^-$: 385.0096; found 385.0102.

10-Bromo-6,6-dimethyl-5,6,7,8-tetrahydrophenanthren-9-ol (9d): The title compound was prepared according to the condition B. White solid (51.5 mg, 84%; eluent: 0%-3% ethyl acetate/hexane). **m.p.**= 75-76 °C. ^{1}H NMR (400 MHz, DMSO) δ 9.25 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 2.79 (t, J = 6.3 Hz, 2H), 2.75 (s, 2H), 1.54 (t, J = 6.4 Hz, 2H), 0.98 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 150.85, 132.40, 131.24, 128.81, 126.99, 126.95, 125.91, 124.20, 123.51, 104.41, 34.76, 28.89, 28.42, 22.92. HRMS (ESI): calcd for $C_{16}H_{16}BrO$ [M - H]$^-$: 303.0391; found 303.0371.



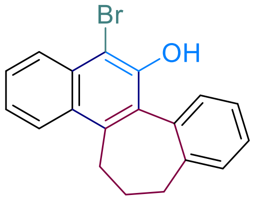
9d

6-Bromo-2-methoxy-11,12-dihydrochrysen-5-ol (9e): The title compound was prepared according to the condition B. White solid (63.9 mg, 90%; eluent: 0%-3% ethyl acetate/hexane). **m.p.**= 83-84 °C. ^{1}H NMR (400 MHz, DMSO) δ 9.48 (s, 1H), 8.23 (d, J = 8.7 Hz, 1H), 8.06 (dd, J = 17.9, 8.4 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.40 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 2.6 Hz, 1H), 6.87 (dd, J = 8.7, 2.7 Hz, 1H), 3.80 (s, 3H), 3.13 – 3.03 (m, 2H), 2.83 – 2.73 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 158.86, 149.67, 140.24, 135.43, 131.50, 130.16, 127.90, 127.72, 126.18, 126.10, 125.56, 124.74, 124.55, 113.08, 111.86, 108.01, 55.54, 29.24, 24.93. HRMS (ESI): calcd for $C_{19}H_{14}BrO$ [M - H]$^-$: 353.0183; found 353.0183.



9e

9-Bromo-2,3-dihydro-1*H*-benzo[3,4]cyclohepta[1,2-*a*]naphthalen-8-ol (9f): The title compound was prepared according to the condition B. Light yellow oil (63.5 mg, 94%; eluent: 0%-3% ethyl acetate/hexane). ^{1}H NMR (400 MHz, DMSO) δ 9.16 (s, 1H), 8.16 – 8.05 (m, 2H), 7.59 – 7.52 (m, 2H), 7.44 – 7.38 (m, 1H), 7.35 – 7.23 (m, 3H), 3.41 – 3.28 (m, 1H), 2.52 (d, J = 11.1 Hz, 1H), 2.23 – 2.03 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ 149.34, 140.20, 136.84, 136.58, 132.45, 130.84, 130.10, 128.59, 128.25, 127.95, 127.55, 126.30, 126.06, 124.93, 124.79, 106.94, 33.20, 31.14, 25.62. HRMS (ESI): calcd for $C_{19}H_{14}BrO$ [M - H]$^-$: 337.0234; found 337.0235.



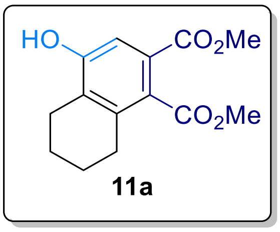
9f

VII. Syntheses of substituted phenols

Condition A: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **3** (0.1 mmol), Dimethyl acetylenedicarboxylate (0.3 mmol, 37 μL) and Benzene (1 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at pre-heated 120 °C heating mantle for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (20 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **11**.

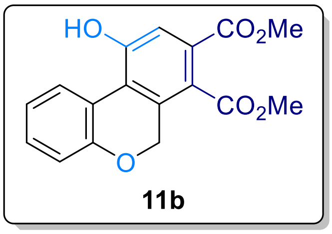
Condition B: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with **3** (0.1 mmol), ethyl 4,4,4-trifluorobut-2-ynoate (0.5 mmol, 71 μL) and THF (1 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at pre-heated 120 °C heating mantle for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (20 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **11**.

Dimethyl 4-hydroxy-5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylate (11a): The title compound was prepared according to the condition A. Light yellow solid (17.6 mg, 67%; eluent: 15%-30% ethyl acetate/hexane). **m.p.**= 108-109 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.19 (s, 1H), 6.46 (s, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 2.71 – 2.62 (m, 4H), 1.80 – 1.70 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 170.84, 166.57, 154.33, 136.27, 129.92, 127.60, 125.50, 113.05, 52.56, 52.46, 26.59, 23.48, 22.17, 21.73. HRMS (ESI): calcd for $C_{14}H_{15}O_5$ [M - H]$^-$: 263.0926; found 263.0925.



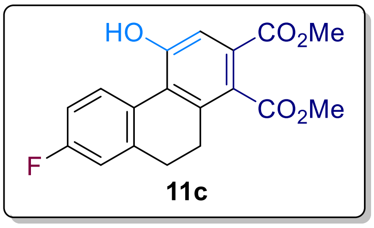
11a

Dimethyl 10-hydroxy-6*H*-benzo[c]chromene-7,8-dicarboxylate (11b): The title compound was prepared according to the condition A. White solid (22.4 mg, 71%; eluent: 15%-30% ethyl acetate/hexane). **m.p.**= 152-153 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.12 (s, 1H), 8.46 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46 (s, 1H), 7.30 (td, *J* = 8.0, 1.6 Hz, 1H), 7.10 (td, *J* = 8.0, 1.3 Hz, 1H), 7.02 (dd, *J* = 8.1, 1.1 Hz, 1H), 4.96 (s, 2H), 3.83 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 167.93, 166.32, 155.55, 155.20, 133.10, 130.34, 129.36, 129.23, 122.36, 122.10, 121.15, 120.39, 117.17, 117.04, 65.82, 53.18, 53.07. HRMS (ESI): calcd for $C_{17}H_{13}O_6$ [M - H]$^-$: 313.0718; found 313.0717.



11b

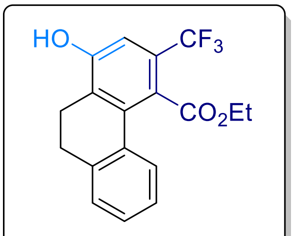
Dimethyl 7-fluoro-4-hydroxy-9,10-dihydrophenanthrene-1,2-dicarboxylate (11c): The title compound was prepared according to the condition A. Yellow solid (20.2 mg, 61%; eluent: 15%-30% ethyl acetate/hexane). **m.p.** = 164-165 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.74 (s, 1H), 8.43 (dd, *J* = 8.8, 6.1 Hz, 1H), 7.46 (s, 1H), 7.14 (ddd, *J* = 20.4, 9.1, 2.7 Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 2.77 – 2.70 (m, 2H), 2.68 – 2.61 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 169.25, 166.01, 162.83, 160.39, 155.28, 141.69 (d, *J* = 8.0 Hz), 137.75, 131.25 (d, *J* = 8.4 Hz), 128.03 (d, *J* = 2.9 Hz), 127.35, 125.04 (d, *J* = 70.3 Hz), 116.21, 114.49 (d, *J* = 21.4 Hz),



11c

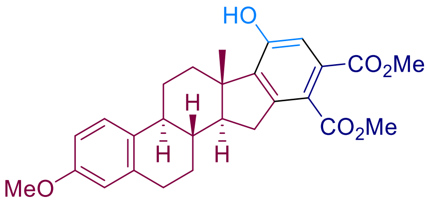
113.23 (d, J = 20.8 Hz), 53.02, 52.77, 28.63, 26.48.^{19}F NMR (377 MHz, DMSO) δ -113.60. HRMS (ESI): calcd for $C_{18}H_{14}FO_5$ [M - H]$^-$: 329.0832; found 329.0828.

Ethyl 1-hydroxy-3-(trifluoromethyl)-9,10-dihydrophenanthrene-4-carboxylate (11d): The title compound was prepared according to the condition B. White solid (29.6 mg, 88%; eluent: 5%-15% ethyl acetate/hexane). **m.p.**= 106-107 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.69 (s, 1H), 7.43 (dd, J = 7.4, 1.5 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.31 – 7.28 (m, 1H), 7.28 – 7.24 (m, 1H), 7.21 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.72 (s, 4H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 168.72, 155.31, 139.27, 135.74, 132.76, 130.66, 128.83, 128.45, 127.01, 126.29 (q, J = 30.9 Hz), 126.27, 124.06 (q, J = 274.7 Hz), 120.63 (q, J = 1.5 Hz), 111.50 (q, J = 4.3 Hz), 61.98, 28.21, 21.97, 13.86. ^{19}F NMR (377 MHz, DMSO) δ -58.01. HRMS (ESI): calcd for $C_{18}H_{14}F_3O_3$ [M - H]$^-$: 335.0901; found 335.0899.



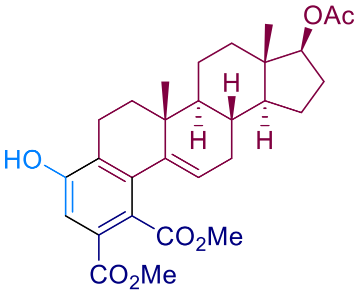
11d

Dimethyl (6b*S*,8a*S*,13a*S*,13b*S*)-9-hydroxy-4-methoxy-8a-methyl-2,6b,7,8,8a,13,13a,13b-octahydro-1*H*-indeno[2,1-*a*]phenanthrene-11,12-dicarboxylate (11e): The title compound was prepared according to the condition A. Light yellow solid (34.0 mg, 76%; eluent: 15%-30% ethyl acetate/hexane). **m.p.** = 208-209 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.11 (d, J = 8.6 Hz, 1H), 7.04 (s, 1H), 6.72 (s, 1H), 6.63 (dd, J = 8.6, 2.7 Hz, 1H), 6.56 (d, J = 2.6 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 2.90 – 2.79 (m, 2H), 2.59 – 2.48 (m, 2H), 2.36 – 2.15 (m, 2H), 1.95 – 1.86 (m, 1H), 1.76 (qd, J = 12.4, 5.2 Hz, 2H), 1.66 – 1.53 (m, 2H), 1.46 – 1.33 (m, 1H), 0.91 (s, 3H), 0.83 – 0.73 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 169.45, 168.01, 157.49, 153.53, 145.24, 143.27, 137.85, 132.62, 129.43, 126.12, 122.57, 115.93, 113.88, 111.57, 55.83, 55.26, 52.69, 52.49, 46.28, 44.03, 37.38, 35.43, 31.72, 27.73, 29.68, 26.53, 16.56. HRMS (ESI): calcd for $C_{27}H_{29}O_6$ [M - H]$^-$: 449.1970; found 449.1967.



11e

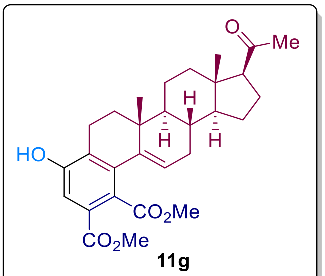
Dimethyl (3*S*,3a*S*,5a*S*,5b*R*,13a*R*,13b*S*)-3-acetoxy-8-hydroxy-3a,5b-dimethyl-2,3,3a,4,5,5a,5b,6,7,13,13a,13b-dodecahydro-1*H*-cyclopenta[*a*]chrysene-10,11-dicarboxylate (11f): The title compound was prepared according to the condition A. Light yellow solid (23.1 mg, 47%; eluent: 15%-30% ethyl acetate/hexane). **m.p.**= 193-194 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.25 (s, 1H), 6.36 (s, 1H), 5.84 (dd, J = 5.5, 2.2 Hz, 1H), 4.66 – 4.60 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.70 (dt, J = 16.9, 7.1 Hz, 1H), 2.54 (dt, J = 17.0, 6.3 Hz, 1H), 2.15 (ddd, J = 18.0, 10.5, 6.1 Hz, 2H), 2.07 (s, 3H), 1.84 – 1.78 (m, 2H), 1.73 (t, J = 6.7 Hz, 2H), 1.70 – 1.48 (m, 6H), 1.41 – 1.32 (m, 1H), 1.14 – 1.03 (m, 2H), 0.93 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 171.62, 170.80, 166.72, 152.66, 140.18, 138.65, 129.63, 127.25, 126.51,



11f

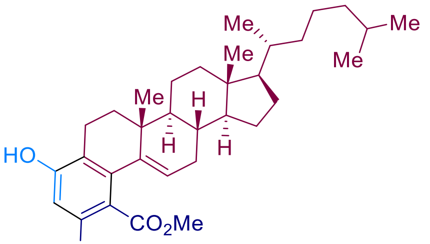
125.36, 114.27, 82.86, 52.49, 52.28, 51.07, 48.84, 42.49, 36.89, 35.22, 32.32, 31.50, 27.57, 23.48, 21.30, 21.24, 20.91, 20.80, 12.05. HRMS (ESI): calcd for $C_{29}H_{35}O_7$ [M - H]$^-$: 495.2389; found 495.2386.

Dimethyl (3*S*,3a*S*,5a*S*,5b*R*,13a*S*,13b*S*)-3-acetyl-8-hydroxy-3a,5b-dimethyl-2,3,3a,4,5,5a,5b,6,7,13,13a,13b-dodecahydro-1*H*-cyclopenta[*a*]chrysene-10,11-dicarboxylate (11g): The title compound was prepared according to the condition A. Light yellow solid (27.5 mg, 57%; eluent: 15%-30% ethyl acetate/hexane). **m.p.** = 184-185 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.19 (s, 1H), 5.78 (dd, *J* = 5.5, 2.3 Hz, 1H), 3.76 (s, 3H), 3.76 (s, 3H), 2.64 (dt, *J* = 17.0, 7.2 Hz, 1H), 2.49 (dt, *J* = 17.0, 6.2 Hz, 2H), 2.19 – 2.10 (m, 1H), 2.08 (s, 3H), 2.03 (ddd, *J* = 18.0, 8.6, 5.5 Hz, 2H), 1.70 – 1.36 (m, 10H), 1.16 – 1.01 (m, 3H), 0.85 (s, 3H), 0.59 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 210.22, 170.88, 166.76, 152.76, 140.12, 138.54, 129.59, 127.26, 126.44, 125.43, 114.25, 63.69, 56.88, 52.50, 52.33, 48.77, 44.15, 38.91, 36.86, 35.25, 32.65, 31.65, 31.56, 24.38, 22.91, 21.80, 20.80, 13.33. HRMS (ESI): calcd for $C_{29}H_{35}O_6$ [M - H]$^-$: 479.2440; found 479.2437.



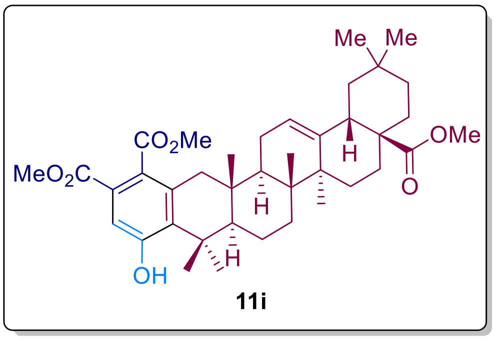
11g

Dimethyl (3*R*,3a*R*,5a*S*,5b*R*,13a*S*,13b*S*)-8-hydroxy-3a,5b-dimethyl-3-((*R*)-6-methylheptan-2-yl)-2,3,3a,4,5,5a,5b,6,7,13,13a,13b-dodecahydro-1*H*-cyclopenta[*a*]chrysene-10,11-dicarboxylate (11h): The title compound was prepared according to the condition A. Brown solid (23.8 mg, 43%; eluent: 15%-30% ethyl acetate/hexane). **m.p.** = 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.43 (s, 1H), 5.76 (dd, *J* = 5.4, 2.2 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 2.60 (dt, *J* = 16.9, 7.1 Hz, 1H), 2.45 (dt, *J* = 17.0, 6.2 Hz, 1H), 2.05 (dt, *J* = 18.4, 5.3 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.83 – 1.71 (m, 1H), 1.63 (t, *J* = 6.7 Hz, 2H), 1.56 – 1.39 (m, 5H), 1.36 – 1.21 (m, 4H), 1.14 – 0.90 (m, 10H), 0.87 – 0.83 (m, 6H), 0.81 (d, *J* = 1.7 Hz, 3H), 0.79 (d, *J* = 1.6 Hz, 3H), 0.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.16, 166.91, 152.74, 140.13, 138.78, 129.78, 127.13, 126.30, 125.86, 114.24, 56.76, 56.18, 52.50, 52.34, 48.87, 42.42, 39.89, 39.53, 36.82, 36.20, 35.81, 35.20, 32.82, 31.68, 28.29, 28.03, 24.18, 23.88, 22.84, 22.59, 21.81, 20.81, 18.75, 11.96. HRMS (ESI): calcd for $C_{35}H_{49}O_5$ [M - H]$^-$: 549.3586; found 549.3586.



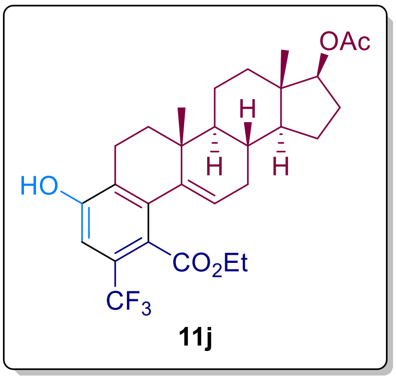
11h

Trimethyl (4a*S*,6a*S*,6b*R*,8a*R*,14a*S*,14b*R*,16b*S*)-10-hydroxy-2,2,6a,6b,9,9,14a-heptamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,14,14a,14b,15,16b-hexadecahydrobenzo[*b*]picene-4a,12,13(2*H*)-tricarboxylate (11i):

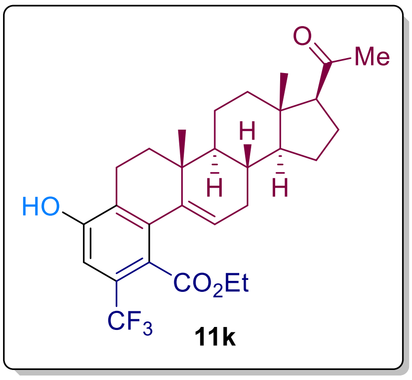

11i

The title compound was prepared according to the condition A. Light yellow solid (31.5 mg, 50%; eluent: 15%-30% ethyl acetate/hexane). **m.p.**= 159-160 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (s, 1H), 5.27 (t, *J* = 3.3 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.58 (s, 3H), 2.83 (dd, *J* = 13.7, 3.9 Hz, 1H), 2.57 (d, *J* = 16.0 Hz, 1H), 2.21 – 2.14 (m, 1H), 1.98 – 1.83 (m, 3H), 1.70 – 1.40 (m, 10H), 1.33 (s, 3H), 1.29 (s, 3H), 1.24 – 1.12 (m, 5H), 1.08 (s, 3H), 0.86 (s, 3H), 0.84 (s, 3H), 0.77 (s, 3H), 0.72 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 178.92, 171.05, 166.30, 155.51, 143.58, 137.19, 134.69, 128.20, 125.43, 122.48, 115.61, 54.58, 52.58, 52.43, 51.78, 46.97, 45.78, 43.57, 41.90, 41.53, 39.21, 37.24, 35.39, 33.89, 33.11, 32.38, 32.18, 30.70, 28.00, 27.67, 25.70, 23.62, 23.32, 23.14, 20.15, 19.66, 16.54, 15.02. HRMS (ESI): calcd for $C_{39}H_{53}O_7$ [M - H]$^-$: 633.3798; found 633.3795.

Ethyl (3*S*,3a*S*,5a*S*,5b*R*,13a*R*,13b*S*)-3-acetoxy-8-hydroxy-3a,5b-dimethyl-10-(trifluoromethyl)-2,3,3a,4,5,5a,5b,6,7,13,13a,13b-dodecahydro-1*H*-cyclopenta[*a*]chrysene-11-carboxylate (11j): The title compound was prepared according to the condition B. White solid (33.3 mg, 64%; eluent: 15%-30% ethyl acetate/hexane). **m.p.**= 206-207 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.93 (s, 1H), 5.77 (dd, *J* = 5.3, 2.0 Hz, 1H), 4.55 (t, *J* = 8.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.66 – 2.57 (m, 1H), 2.49 (dt, *J* = 12.2, 5.9 Hz, 1H), 2.18 – 2.04 (m, 2H), 2.00 (s, 3H), 1.79 – 1.36 (m, 10H), 1.35 – 1.26 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (ddd, *J* = 16.4, 9.9, 2.8 Hz, 1H), 1.06 – 0.91 (m, 2H), 0.86 (s, 3H), 0.75 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 172.06, 169.31, 153.12, 140.53, 139.51, 128.30, 126.36 (q, *J* = 31.7 Hz), 125.94, 123.53 (q, *J* = 274.9 Hz), 123.14 (q, *J* = 1.8 Hz), 110.65 (q, *J* = 4.7 Hz), 83.03, 61.61, 50.96, 48.84, 42.49, 36.83, 36.79, 35.23, 32.21, 31.55, 27.50, 23.47, 21.26, 20.67, 20.57, 13.89, 11.99. ^{19}F NMR (377 MHz, CDCl$_3$) δ -59.22. HRMS (ESI): calcd for $C_{29}H_{34}F_3O_5$ [M - H]$^-$: 519.2365; found 519.2361.

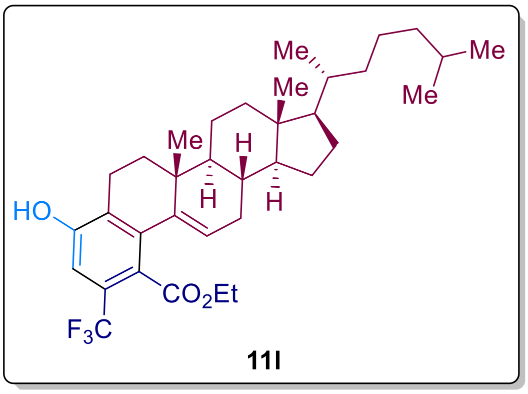

11j

Ethyl (3*S*,3a*S*,5a*S*,5b*R*,13a*S*,13b*S*)-3-acetyl-8-hydroxy-3a,5b-dimethyl-10-(trifluoromethyl)-2,3,3a,4,5,5a,5b,6,7,13,13a,13b-dodecahydro-1*H*-cyclopenta[*a*]chrysene-11-carboxylate (11k): The title compound was prepared according to the condition B. White solid (31.8 mg, 63%; eluent: 15%-30% ethyl acetate/hexane). **m.p.** = 186-187 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.39 (s, 1H), 7.05 (s, 1H), 5.80 – 5.64 (m, 1H), 4.21 – 4.08 (m, 2H), 2.71 – 2.52 (m, 3H), 2.08 (s, 3H), 2.04 (d, *J* = 5.2 Hz, 3H), 1.77 – 1.55 (m, 6H), 1.53 – 1.38 (m, 3H), 1.19 (t, *J* = 6.6 Hz, 3H), 1.17 – 1.00 (m, 3H), 0.84 (s, 3H), 0.57 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 208.85, 168.34, 154.80, 140.67, 139.12, 128.86, 125.66, 125.23 (q, *J* = 30.9 Hz), 124.06 (q, *J* = 274.52 Hz), 122.09 (q, *J* = 1,8 Hz), 110.07 (q, *J* = 5.1 Hz), 62.96, 61.38, 56.31, 48.59, 43.69, 38.41, 36.69, 35.22, 32.40, 31.71, 31.60, 24.40, 22.72, 21.69, 20.77, 14.11, 13.34. ^{19}F NMR (377 MHz, DMSO) δ -58.10. HRMS (ESI): calcd for $C_{29}H_{34}F_3O_4$ $[M - H]^-$: 503.2415; found 503.2413.



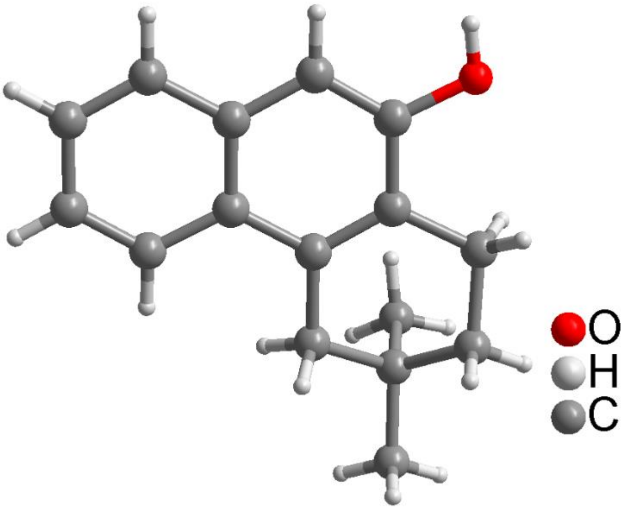
11k

Ethyl (3*R*,3a*R*,5a*S*,5b*R*,13a*S*,13b*S*)-8-hydroxy-3a,5b-dimethyl-3-((*R*)-6-methylheptan-2-yl)-10-(trifluoromethyl)-2,3,3a,4,5,5a,5b,6,7,13,13a,13b-dodecahydro-1*H*-cyclopenta[*a*]chrysene-11-carboxylate (11l): The title compound was prepared according to the condition B. Light yellow solid (41.7 mg, 73%; eluent: 15%-30% ethyl acetate/hexane). **m.p.** = 159-160 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.89 (s, 1H), 6.42 (s, 1H), 5.78 (dd, *J* = 5.3, 2.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.63 – 2.53 (m, 1H), 2.47 (dt, *J* = 17.0, 5.9 Hz, 1H), 2.07 – 1.94 (m, 2H), 1.83 – 1.65 (m, 2H), 1.65 – 1.55 (m, 2H), 1.39 (dddd, *J* = 29.3, 24.2, 13.8, 4.6 Hz, 7H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.20 – 0.88 (m, 11H), 0.85 (d, *J* = 5.4 Hz, 6H), 0.80 (d, *J* = 1.4 Hz, 3H), 0.79 (d, *J* = 1.3 Hz, 3H), 0.61 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 169.73, 152.96, 140.43, 139.68, 128.18, 126.57, 126.49 (q, *J* = 31.6 Hz), 123.49 (q, *J* = 274.8 Hz), 123.12 (q, *J* = 1.9 Hz), 110.59 (q, *J* = 4.9 Hz), 61.78, 56.65, 56.16, 48.91, 42.39, 39.84, 39.53, 36.72, 36.20, 35.81, 35.21, 32.76, 31.76, 28.28, 28.04, 24.20, 23.89, 22.83, 22.58, 21.76, 20.56, 20.50, 18.74, 13.86, 11.91. ^{19}F NMR (377 MHz, CDCl$_3$) δ -59.23. HRMS (ESI): calcd for $C_{35}H_{48}F_3O_3$ $[M - H]^-$: 573.3562; found 573.3559.



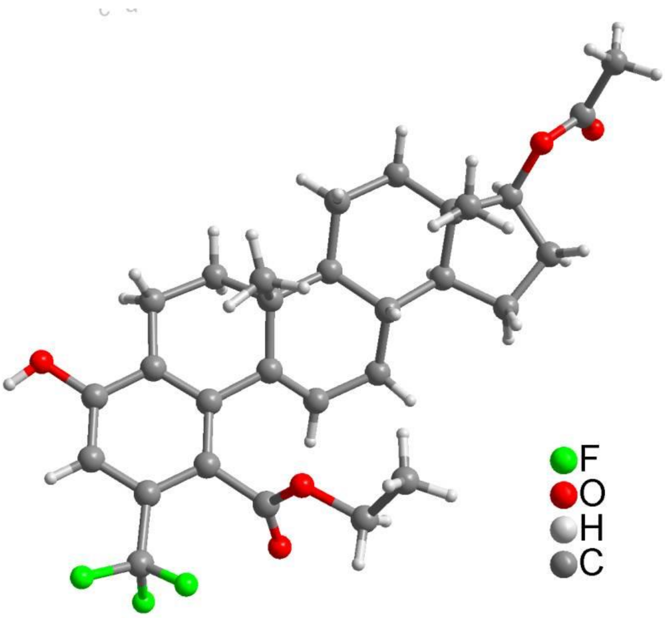
11l

VIII. X-ray crystallographic analysis of 7c (CCDC: 2337021) and 11j (CCDC: 2337023)



Identification code	**7c**
Empirical formula	$C_{16}H_{18}O$
Formula Mass	226.30
Temperature / K	293(2)
Wavelength / Å	1.54184
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	10.3791(2)
b / Å	18.0337(4)
c / Å	7.18597(15)
β / °	109.003(2)
V / Å^3	1271.73(5)
Z	4
μ / mm^{-1}	0.552
$F(000)$	488
Crystal size / mm	0.4 x 0.32 x 0.21
Theta range for data collection / °	4.506 to 76.482
Index ranges	$-13<=h<=13$ $-22<=k<=22$ $-6<=l<=8$
ρ_{calcd} /g cm^{-3}	1.182
Measured refls.	8018
Independent refls.	2560
Completeness to theta = 67.684°	99.8%
Absorption correction	Semi-empirical from equivalents
Ratio of min. to max. transmission	0.87850
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2560/0/158
R_{int}	0.0212
[a]R indices [$I > 2\sigma(I)$] R_1, $wR2$	0.0412, 0.1213

R indices (all data) R_1, $wR2$	0.0467, 0.1266
GOF	1.053
Largest diff. peak and hole / e.Å^{-3}	0.151 and -0.151
CCDC reference numbers	2337021



Identification code	**11j**
Empirical formula	$C_{29}H_{35}F_3O_5$
Formula Mass	520.57
Temperature / K	293(2)
Wavelength / Å	1.54184
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a / Å	10.5004(2)
b / Å	16.0195(2)
c / Å	16.1548(3)
β / °	90
V / Å^3	2717.41(9)
Z	4
μ / mm^{-1}	0.831
F(000)	1104
Crystal size / mm	0.4 x 0.35 x 0.2
Theta range for data collection / °	3.886 to 76.010
Index ranges	$-13<=h<=12$ $-19<=k<=12$ $-20<=l<=20$
ρ_{calcd} /g cm^{-3}	1.272
Measured refls.	10038
Independent refls.	4988

Completeness to theta = 67.684°	99.9 %
Absorption correction	Semi-empirical from equivalents
Ratio of min. to max. transmission	0.95147
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4988/1/340
R_{int}	0.0261
[a]R indices [$I > 2\sigma(I)$] R_1, $wR2$	0.0458, 0.1368
R indices (all data) R_1, $wR2$	0.0521, 0.1456
GOF	1.062
Largest diff. peak and hole / e.Å^{-3}	0.501 and -0.299
CCDC reference numbers	2337023

IX. References

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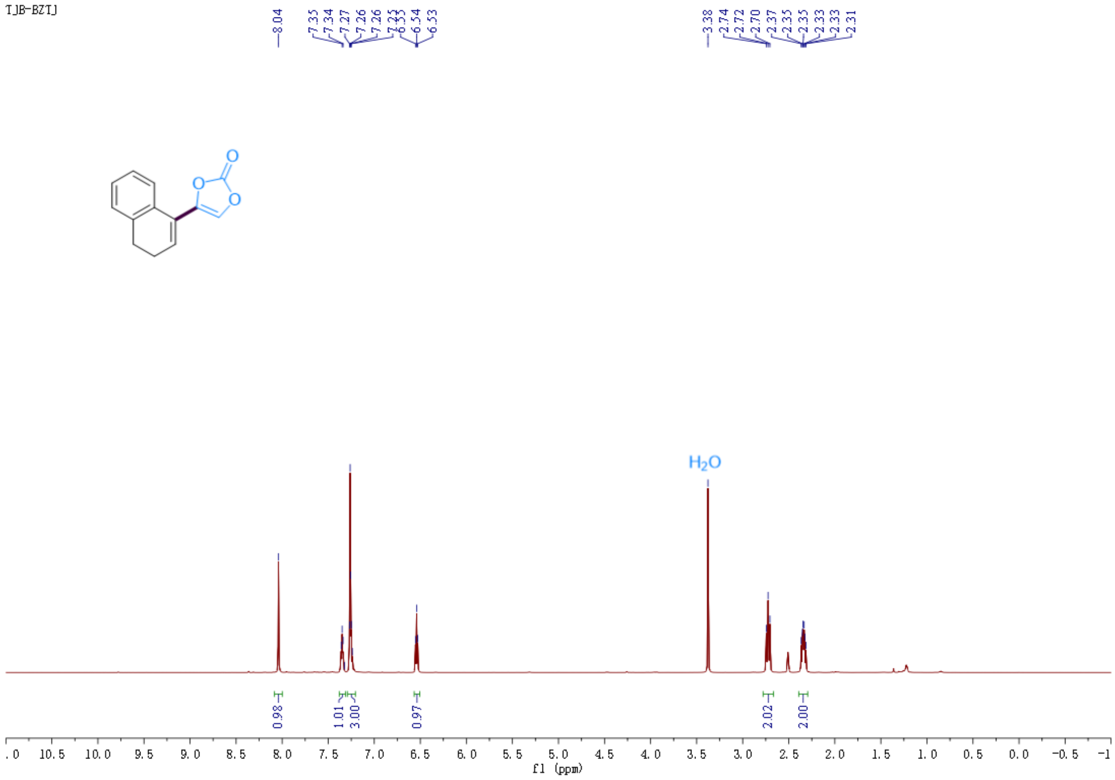
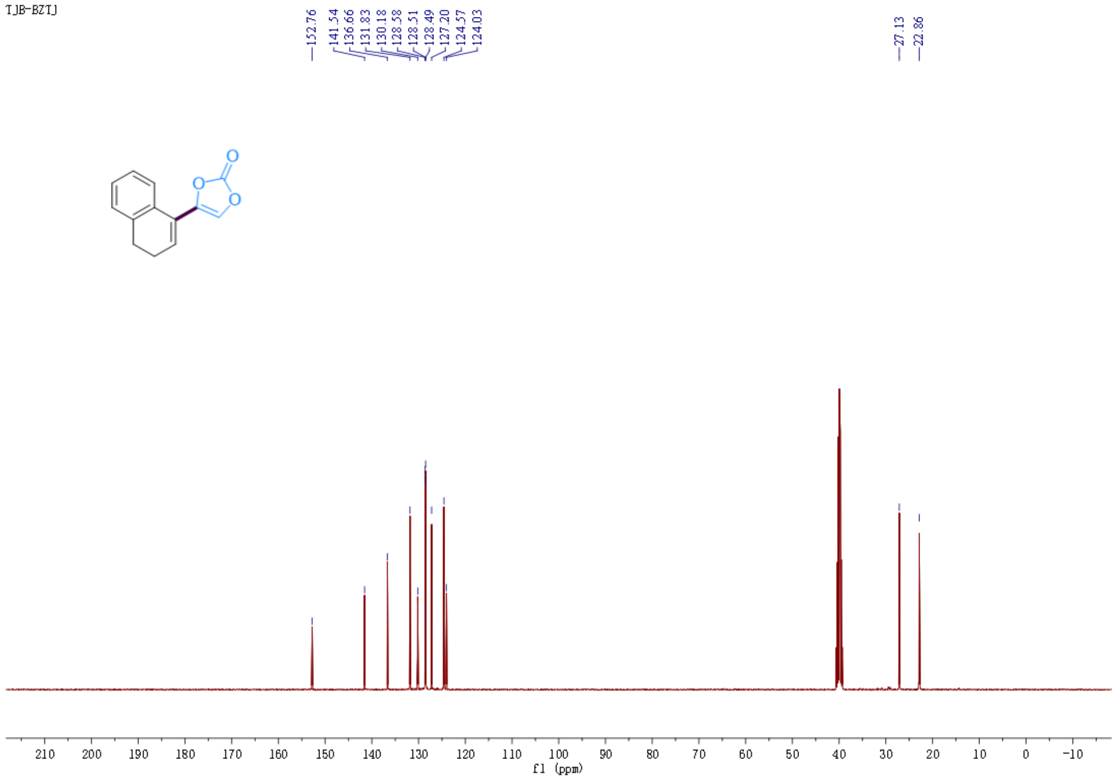
X. ^{1}H, ^{13}C and ^{19}F NMR spectra

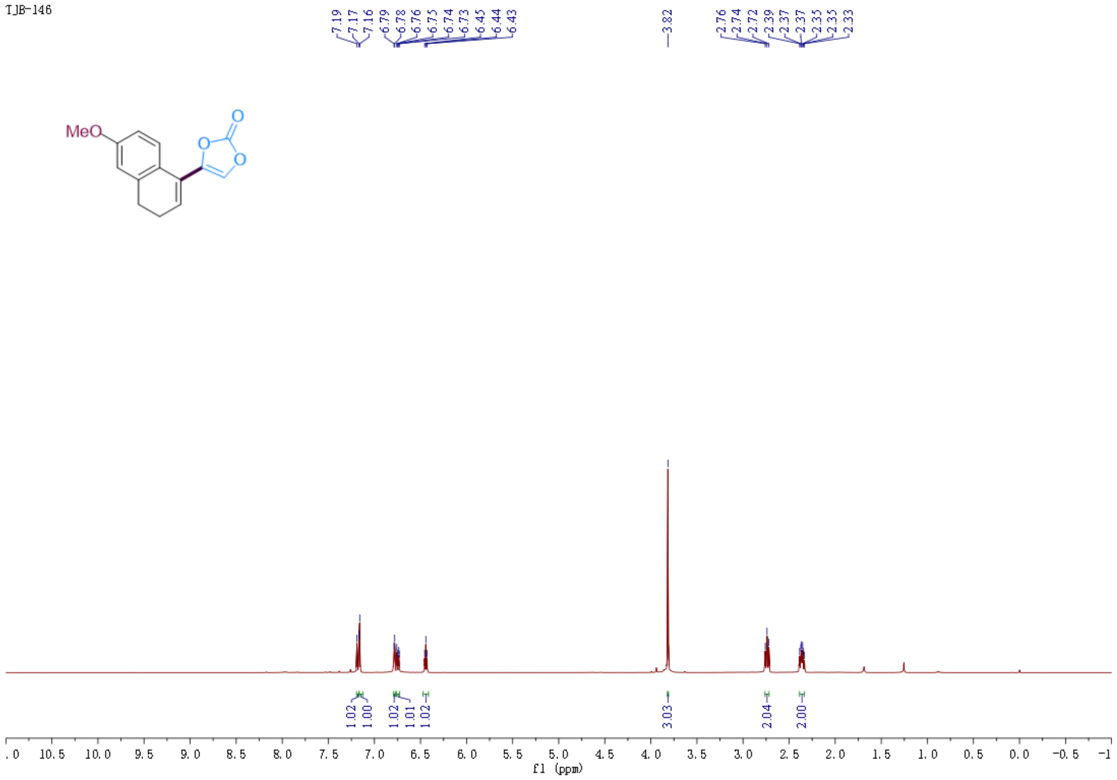
^{1}H NMR spectra of 3a (400 MHz, $(CD_3)_2SO$)



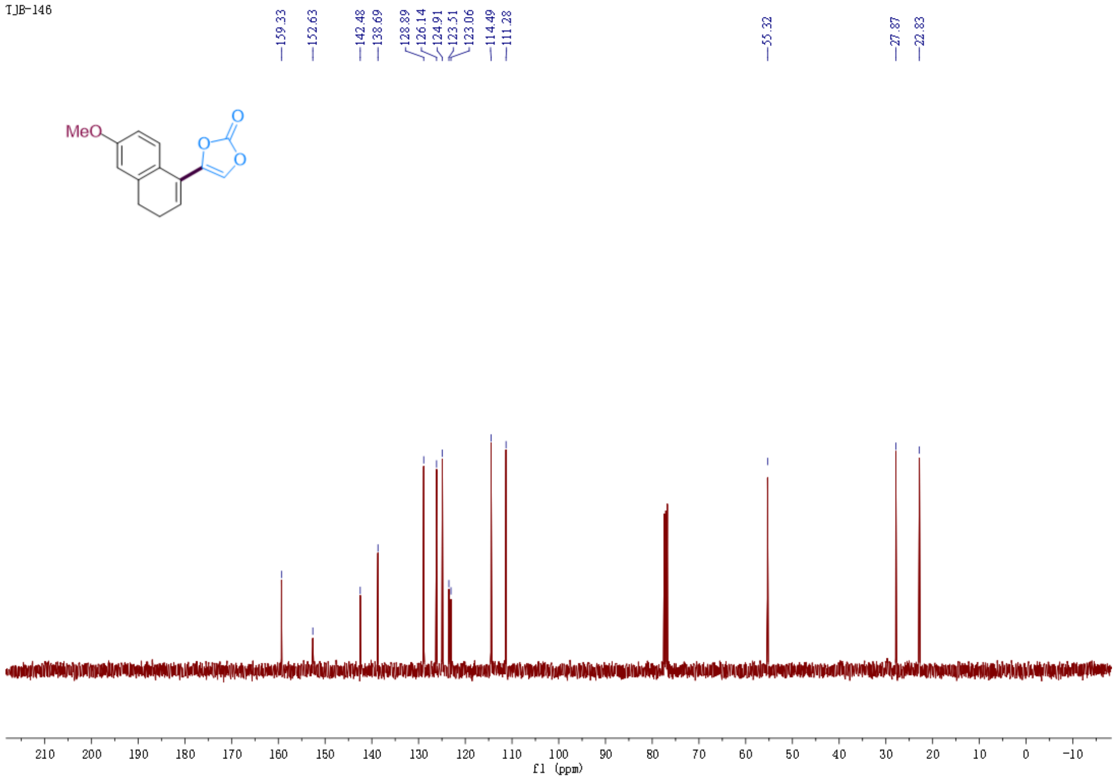
^{13}C NMR spectra of 3a (101 MHz, $(CD_3)_2SO$)



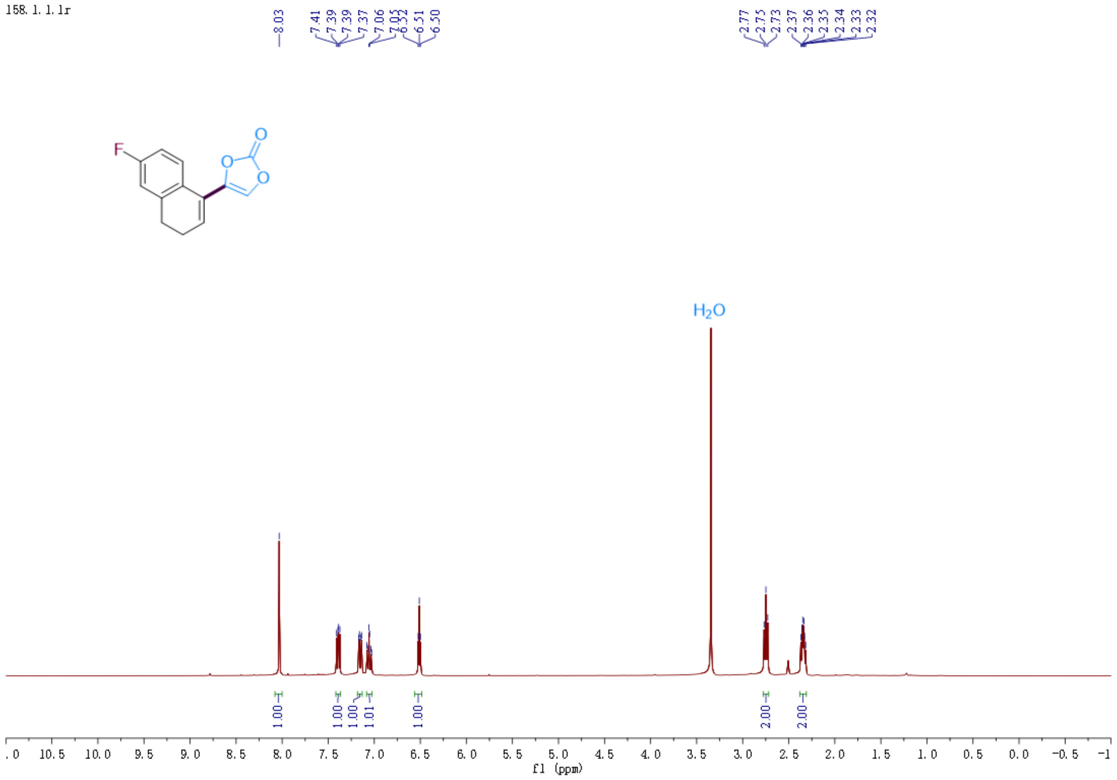
^{1}H NMR spectra of 3b (400 MHz, $CDCl_3$)



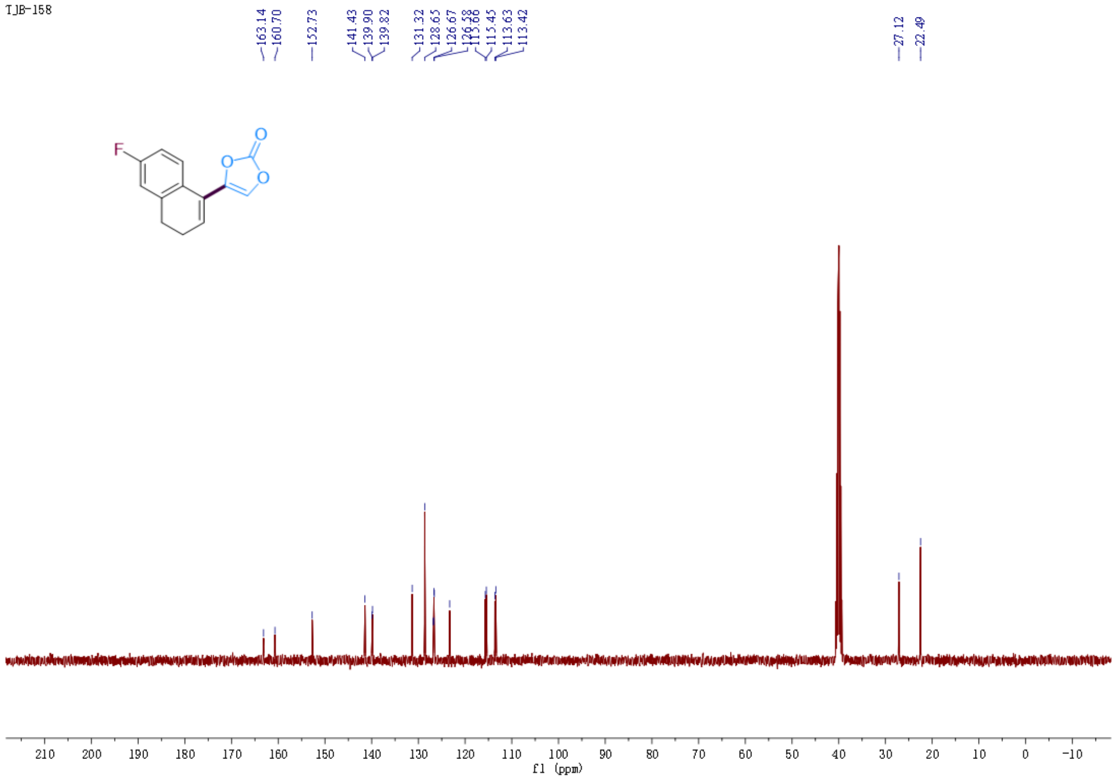
^{13}C NMR spectra of 3b (101 MHz, $CDCl_3$)



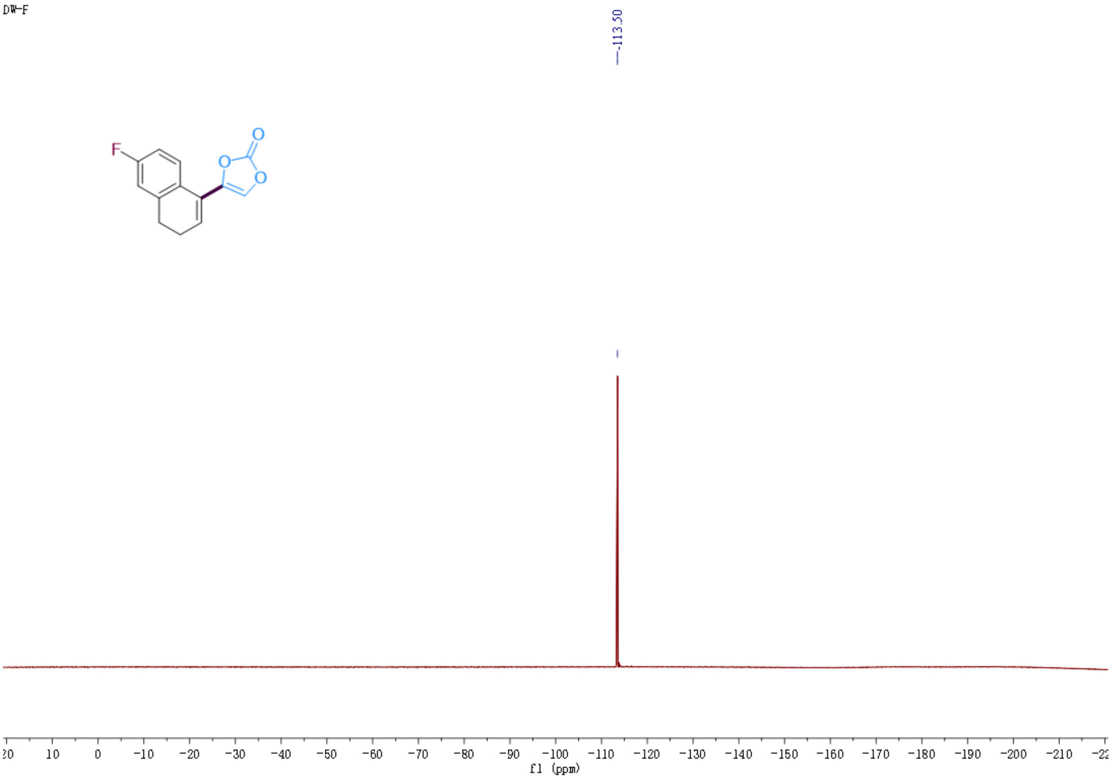
^{1}H NMR spectra of 3c (400 MHz, $(CD_3)_2SO$)



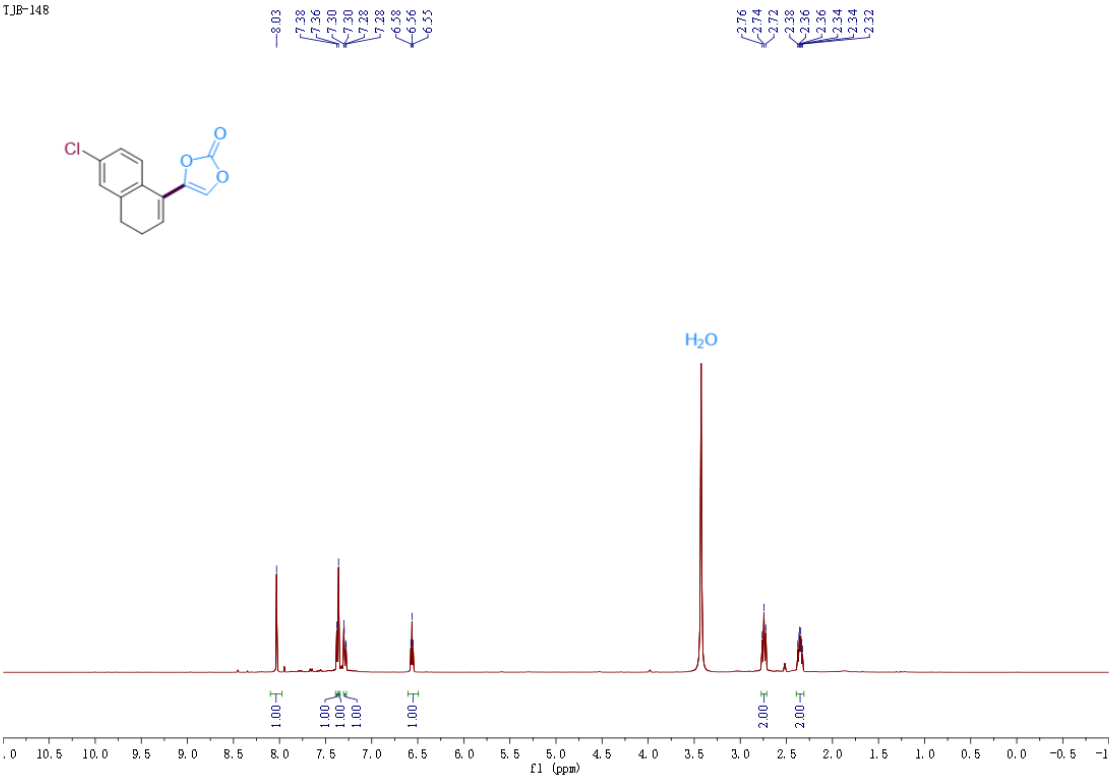
^{13}C NMR spectra of 3c (101 MHz, $(CD_3)_2SO$)



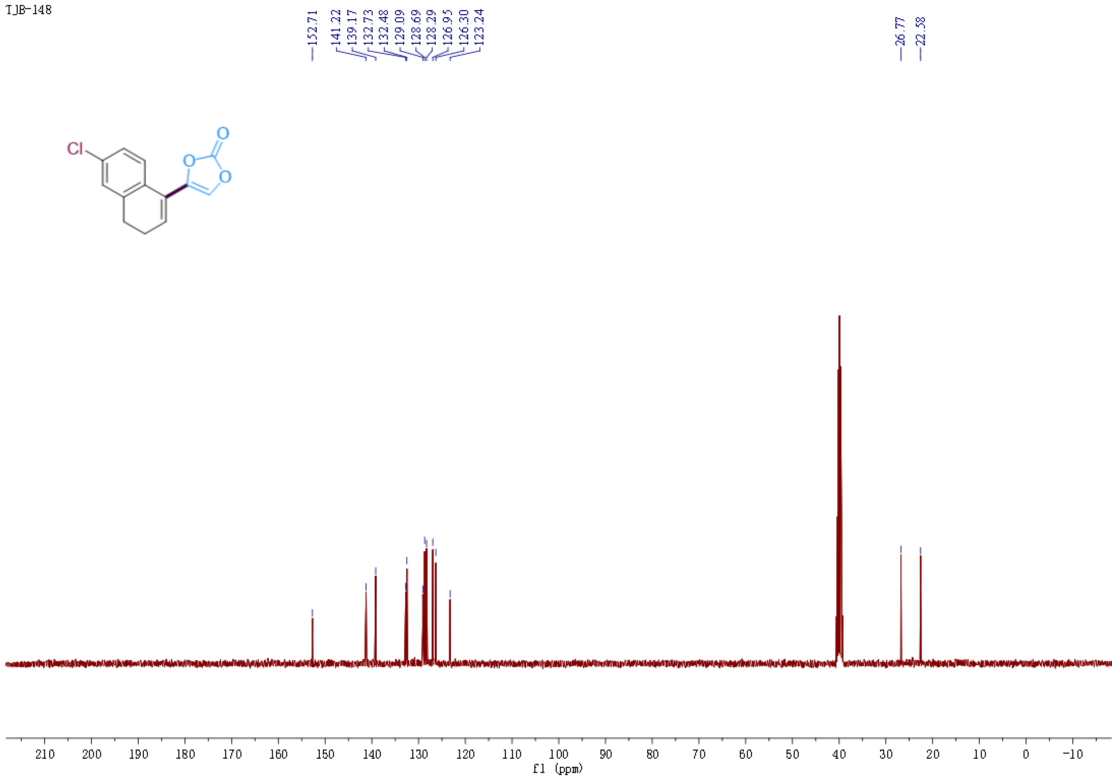
^{19}F NMR NMR spectra of 3c (377 MHz, $(CD_3)_2SO$)



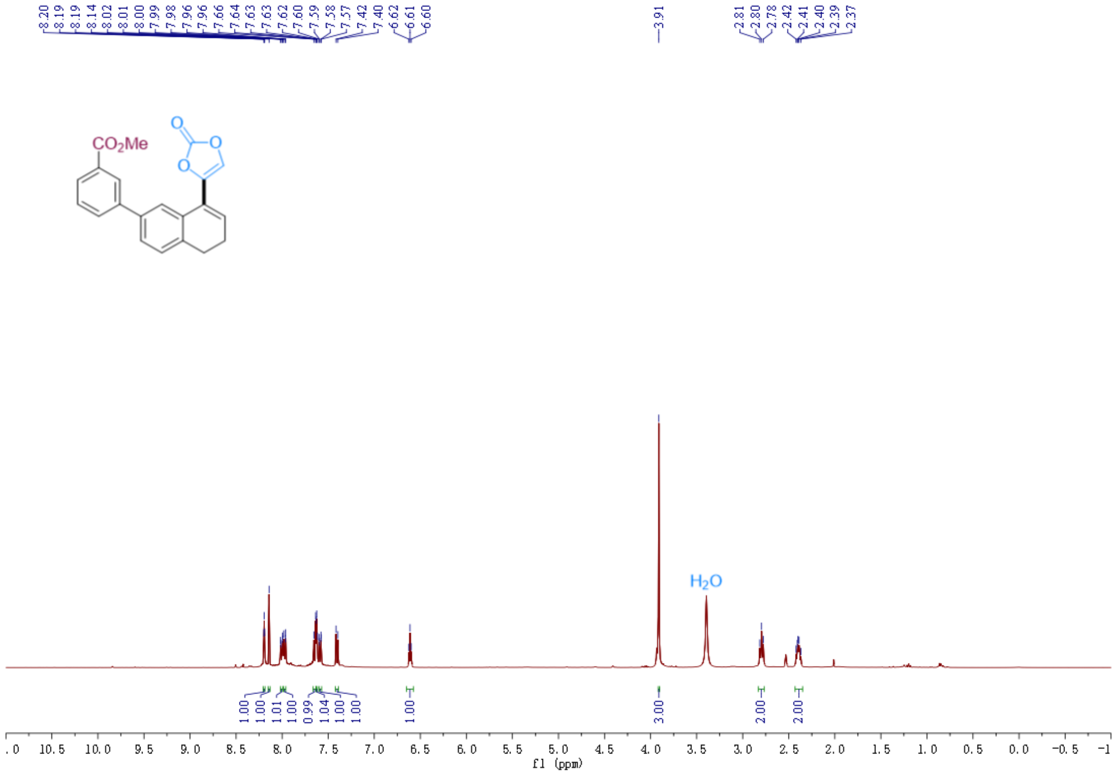
^{1}H NMR spectra of 3d (400 MHz, $(CD_3)_2SO$)



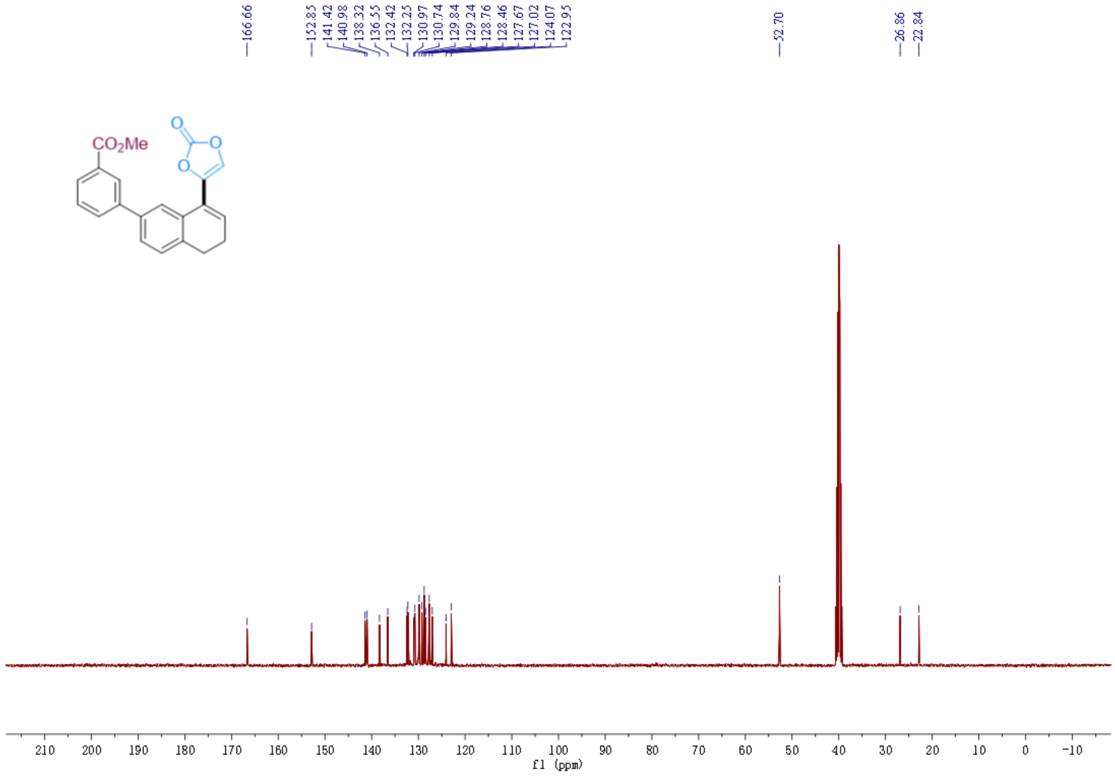
^{13}C NMR spectra of 3d (101 MHz, $(CD_3)_2SO$)



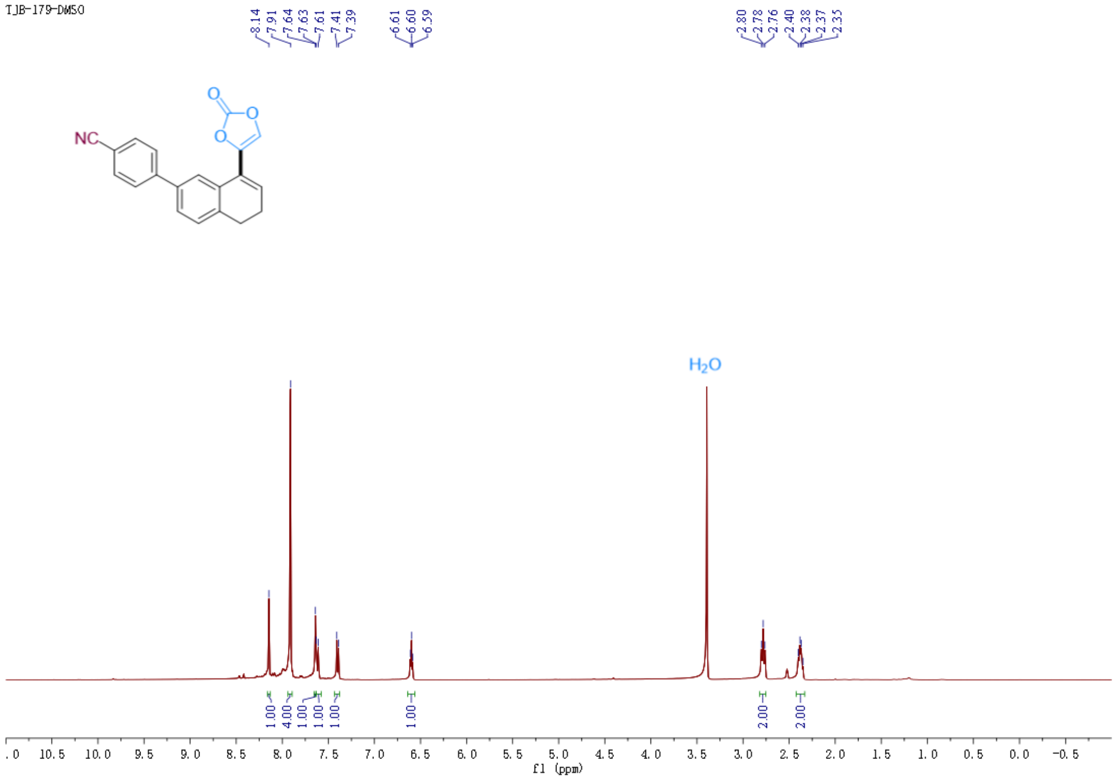
^{1}H NMR spectra of 3e (400 MHz, $(CD_3)_2SO$)



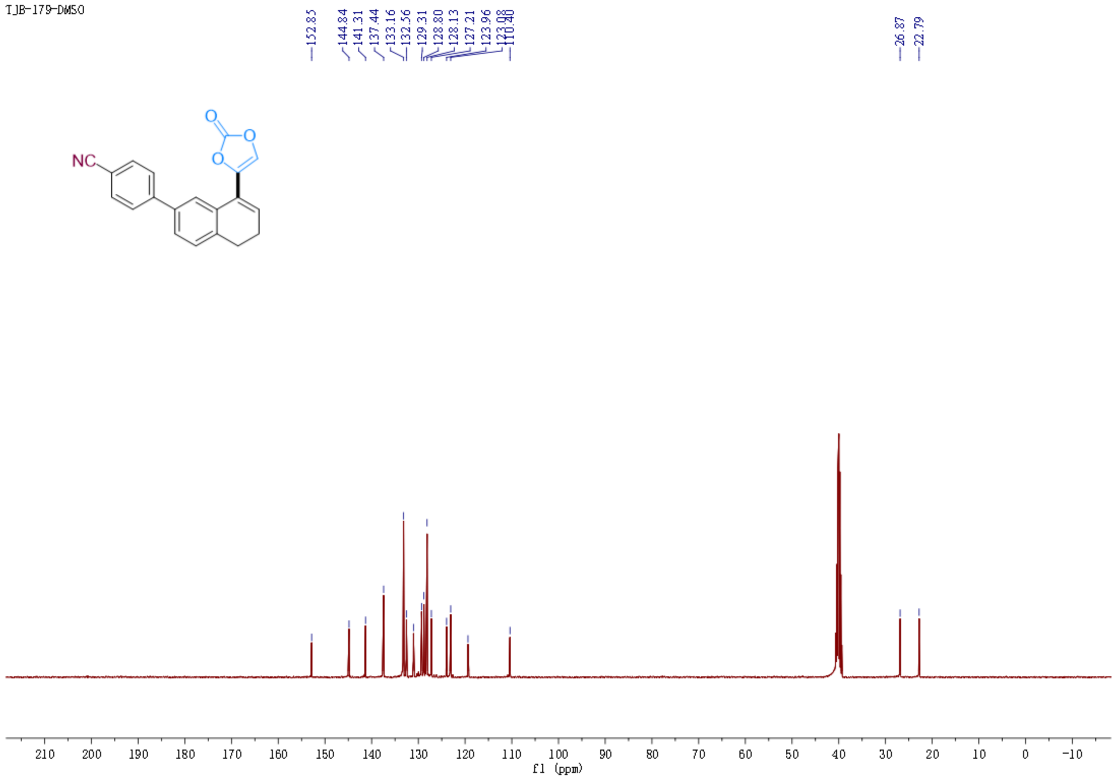
^{13}C NMR spectra of 3e (101 MHz, $(CD_3)_2SO$)



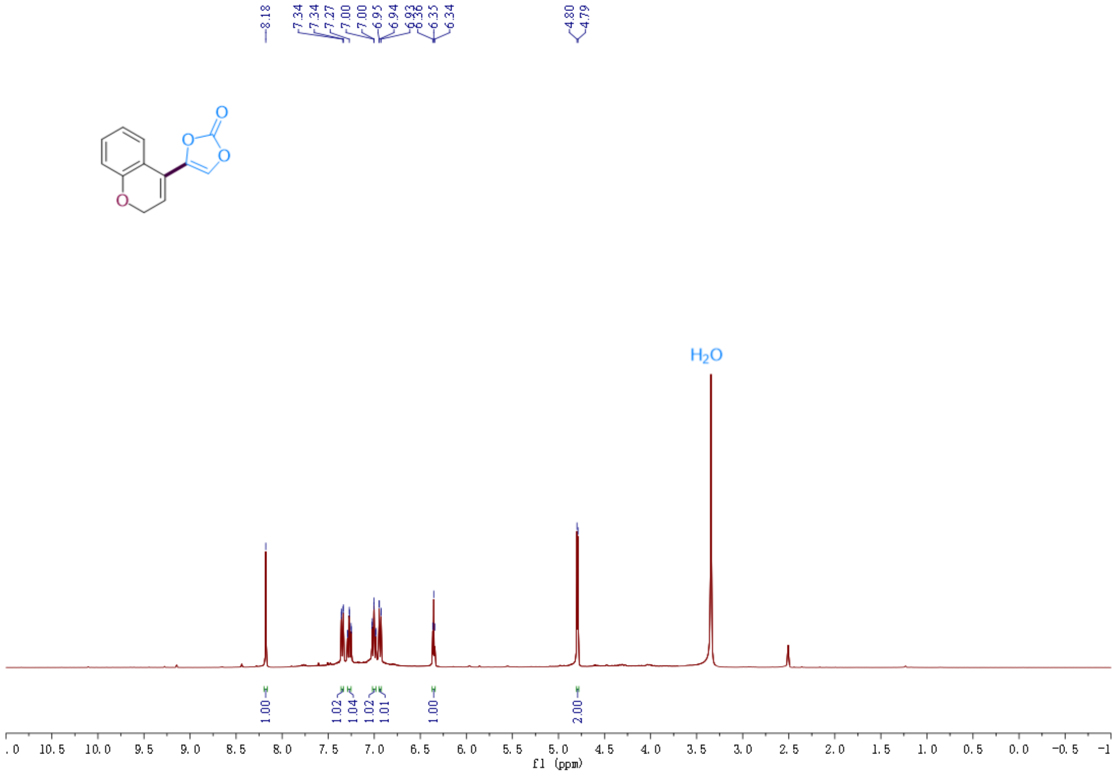
^{1}H NMR spectra of 3f (400 MHz, $(CD_3)_2SO$)



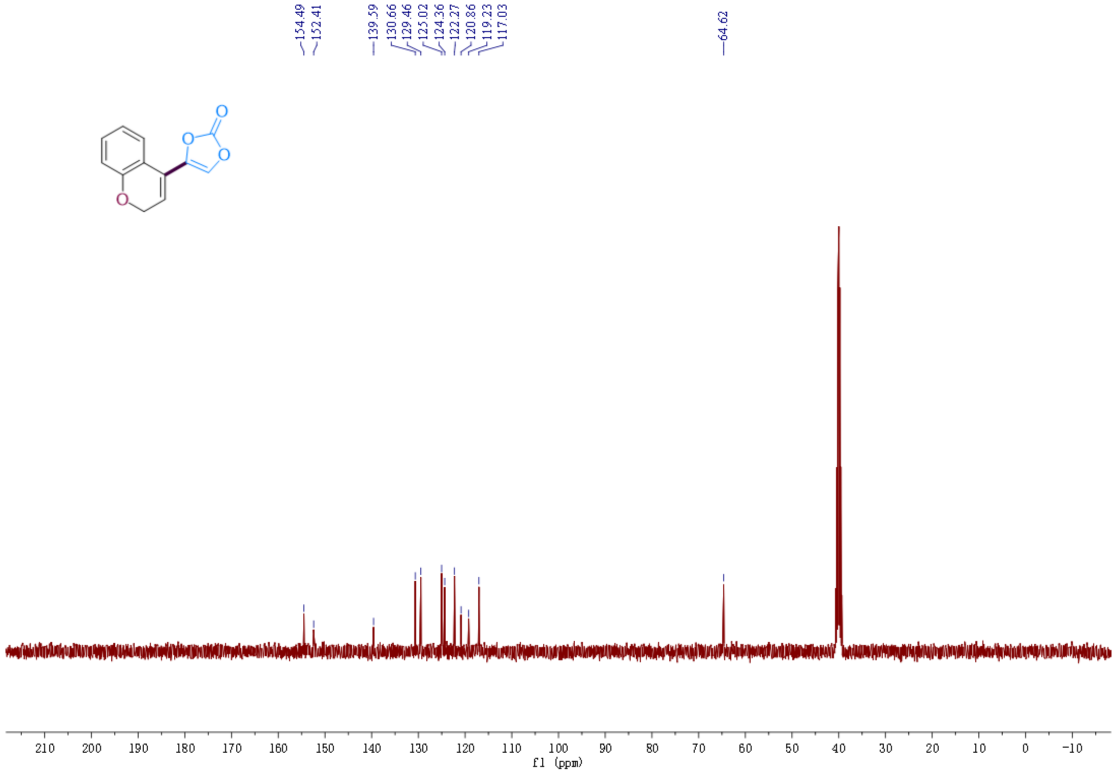
^{13}C NMR spectra of 3f (101 MHz, $(CD_3)_2SO$)



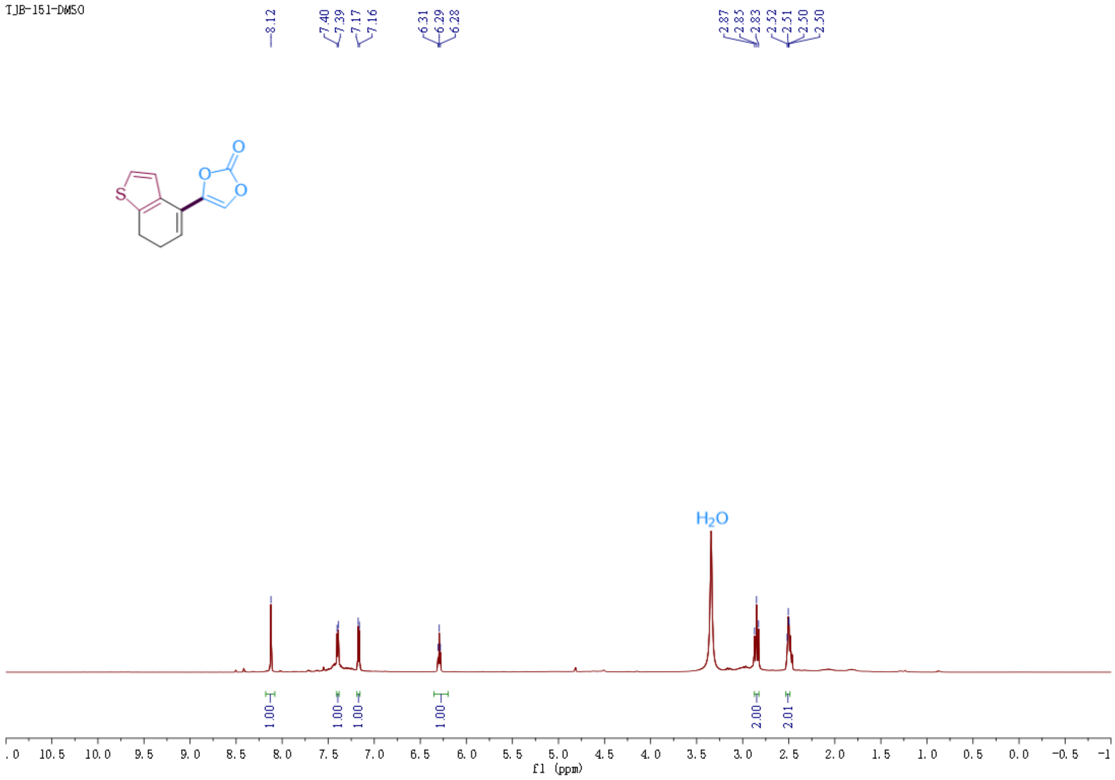
^{1}H NMR spectra of 3g (400 MHz, $(CD_3)_2SO$)



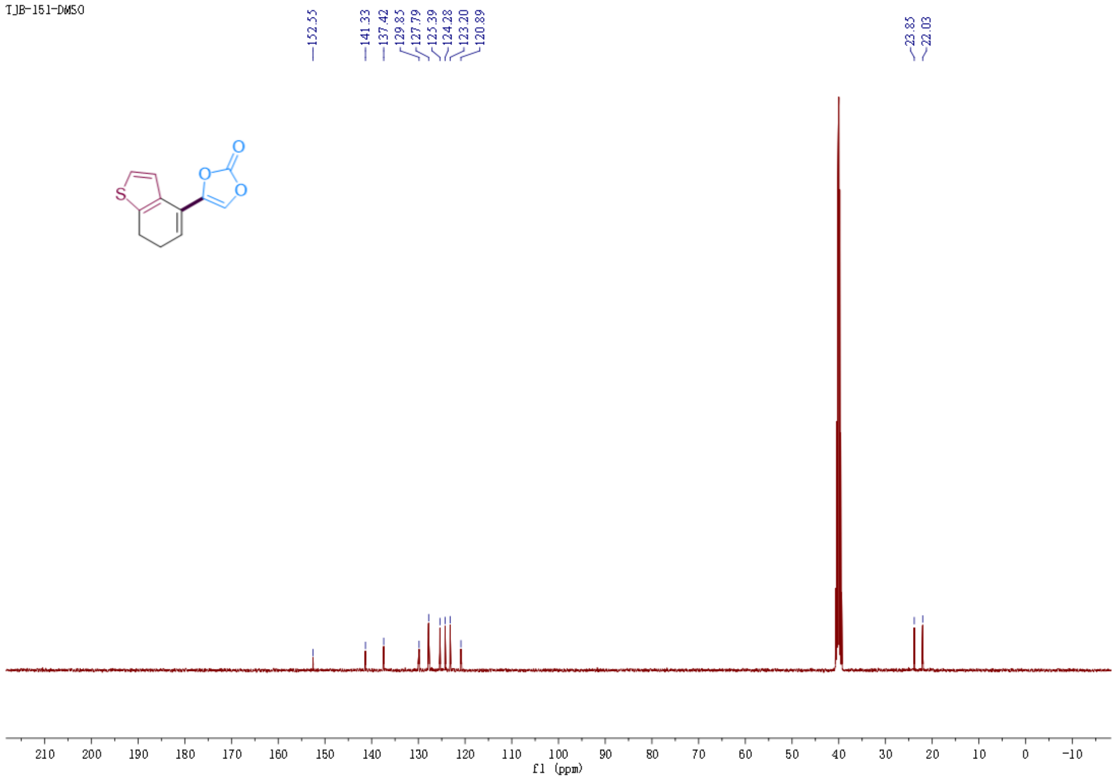
^{13}C NMR spectra of 3g (101 MHz, $(CD_3)_2SO$)



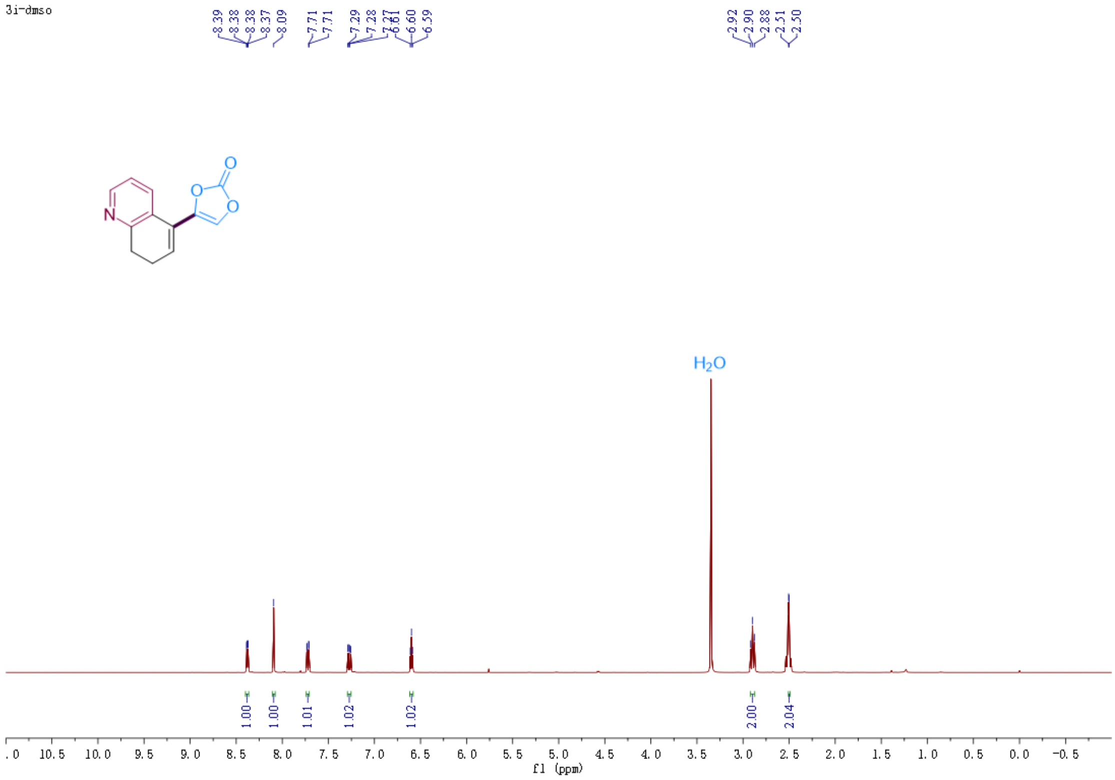
^{1}H NMR spectra of 3h (400 MHz, $(CD_3)_2SO$)



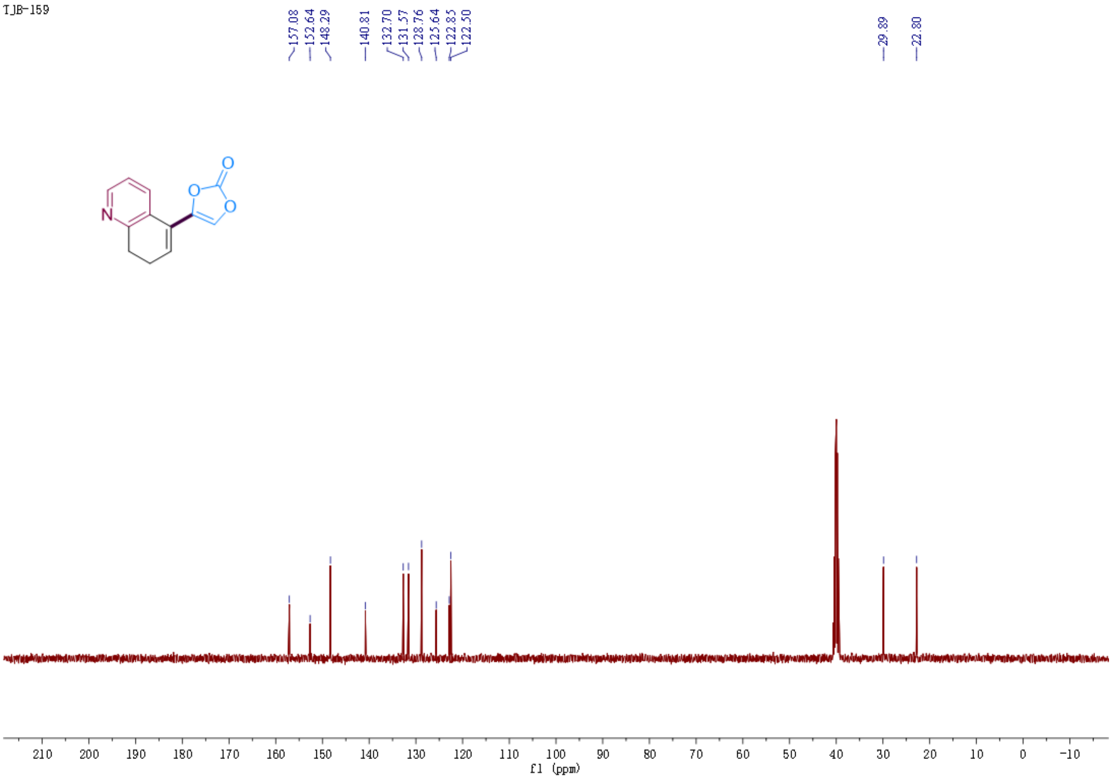
^{13}C NMR spectra of 3h (101 MHz, $(CD_3)_2SO$)



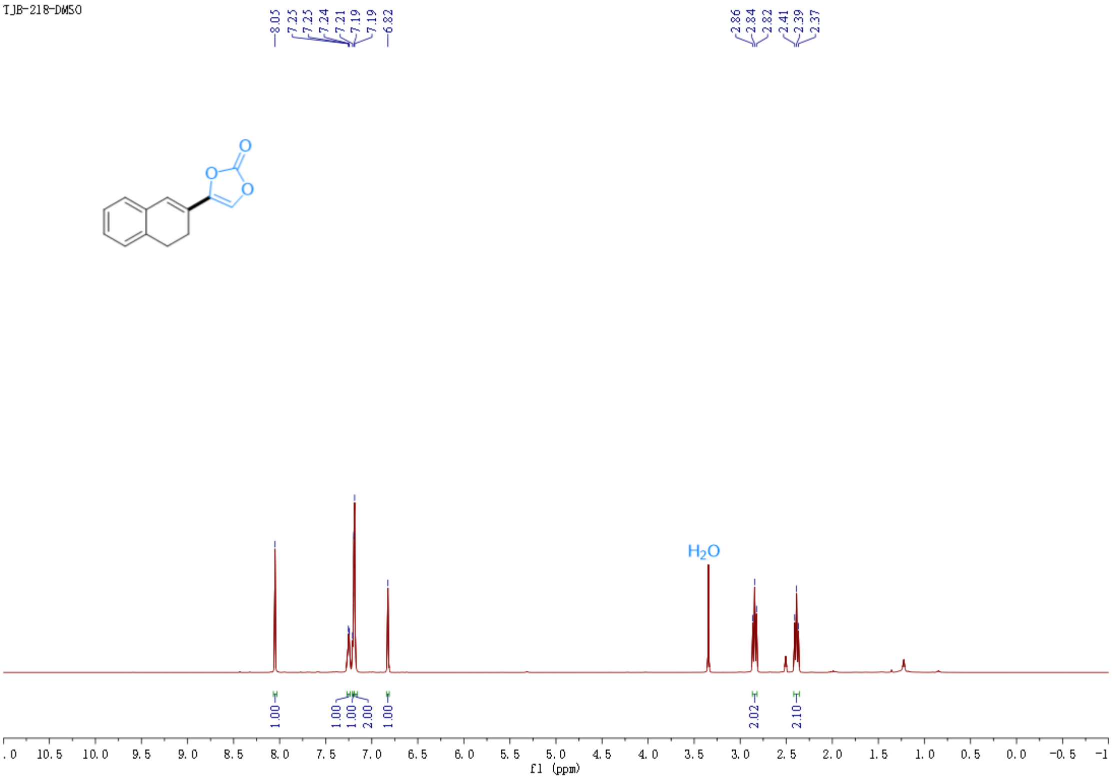
^{1}H NMR spectra of 3i (400 MHz, $(CD_3)_2SO$)



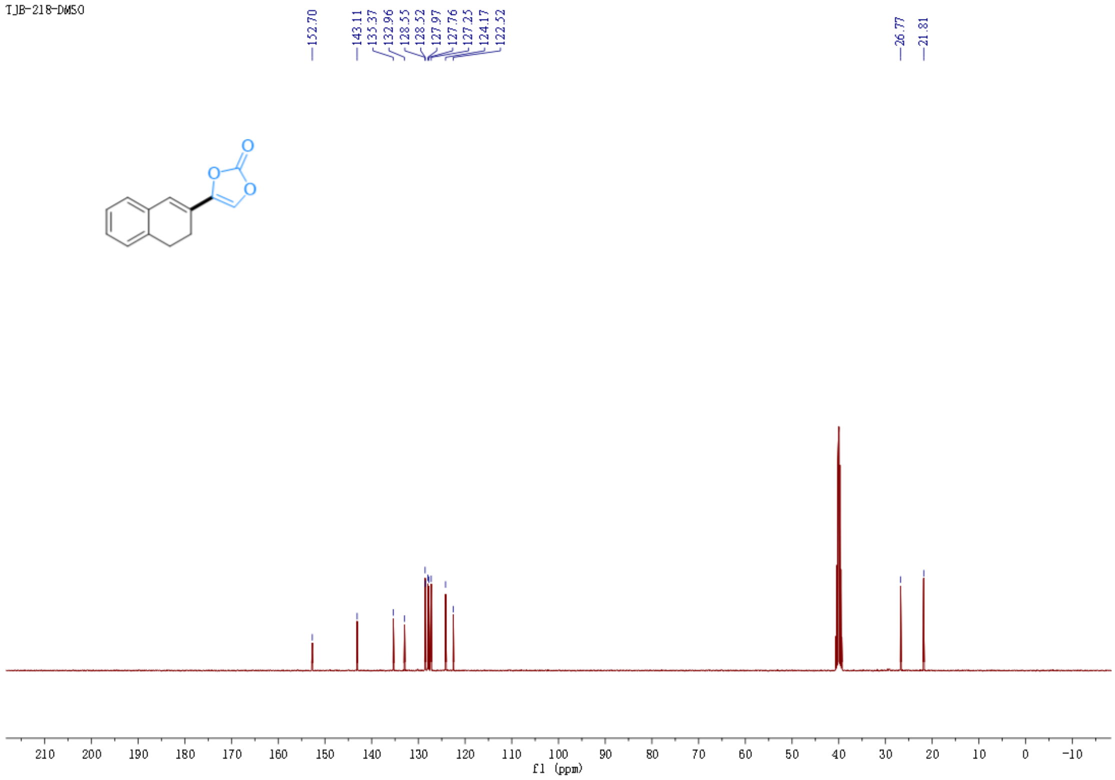
^{13}C NMR spectra of 3i (101 MHz, $(CD_3)_2SO$)



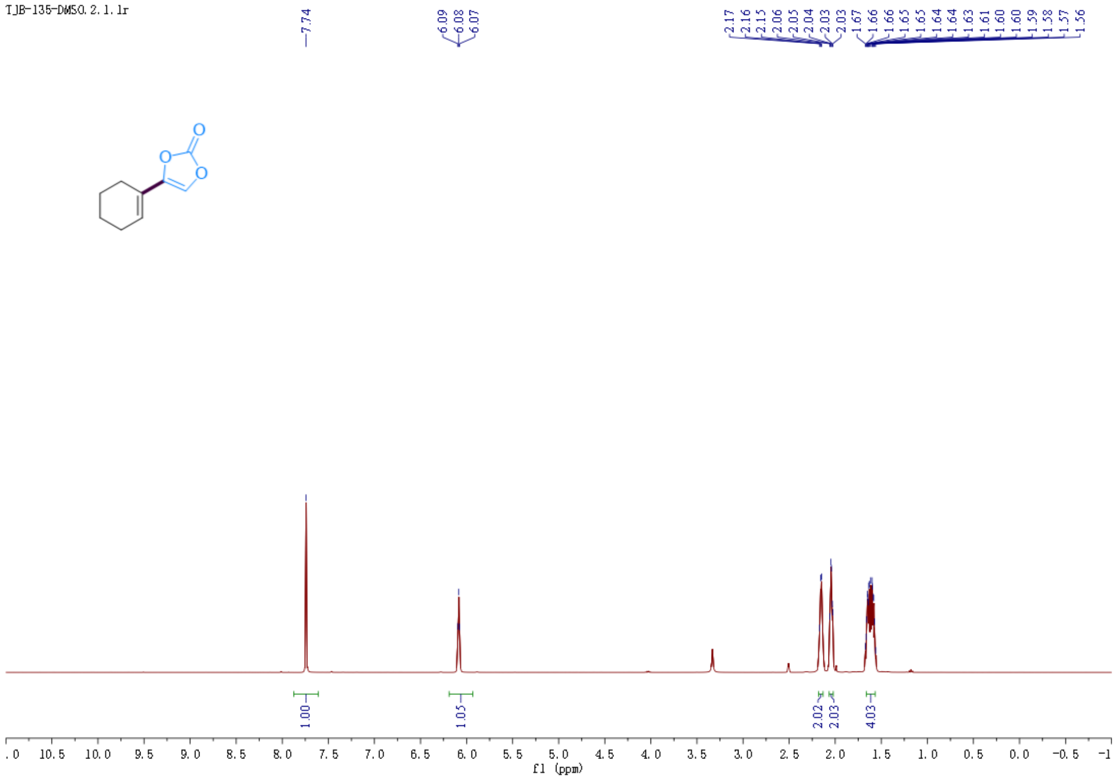
^{1}H NMR spectra of 3j (400 MHz, $(CD_3)_2SO$)



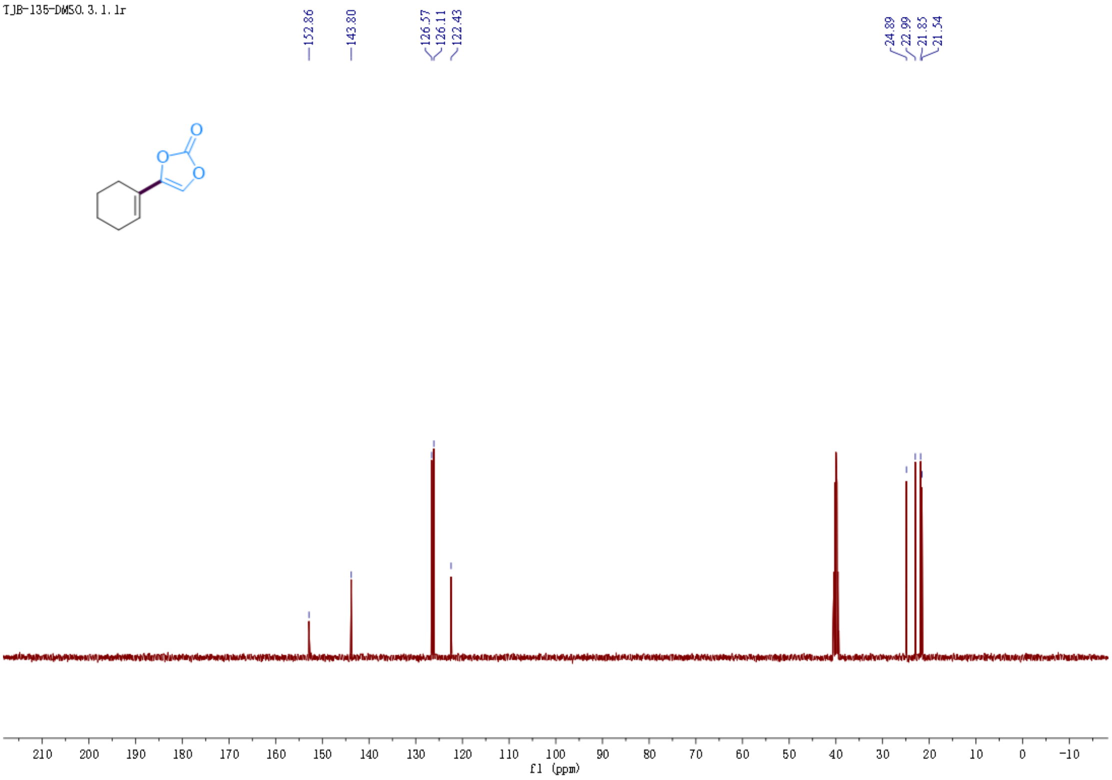
^{13}C NMR spectra of 3j (101 MHz, $(CD_3)_2SO$)



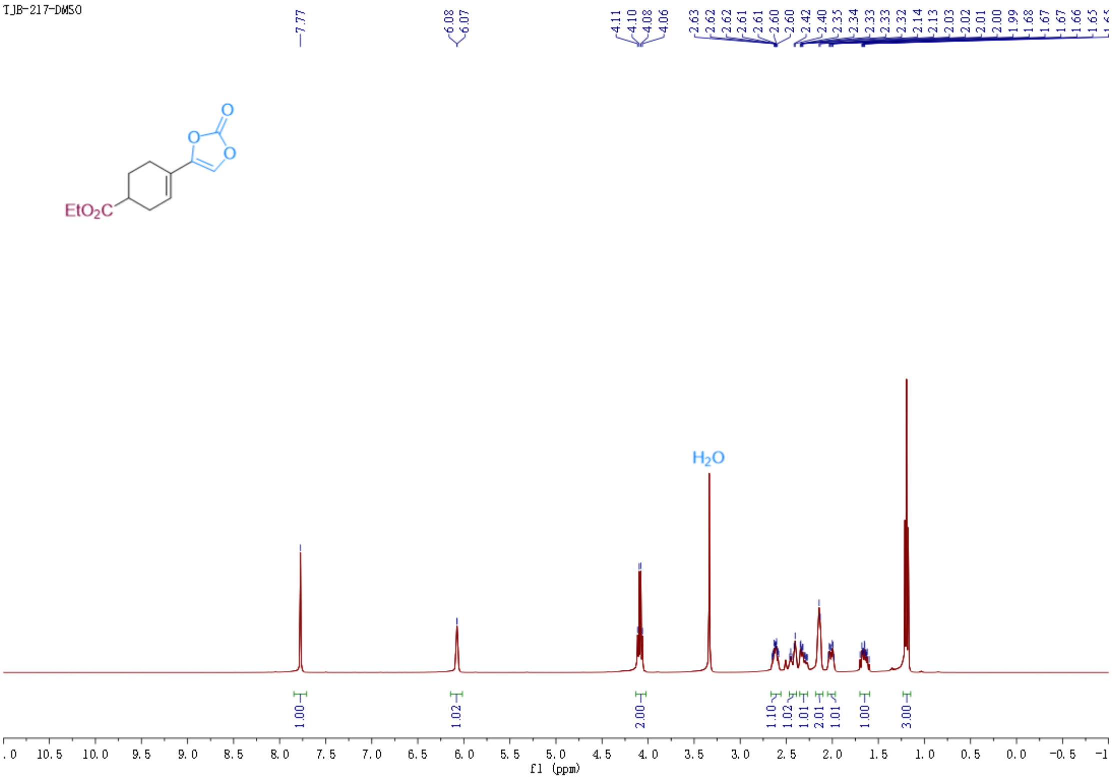
^{1}H NMR spectra of 3k (400 MHz, $(CD_3)_2SO$)



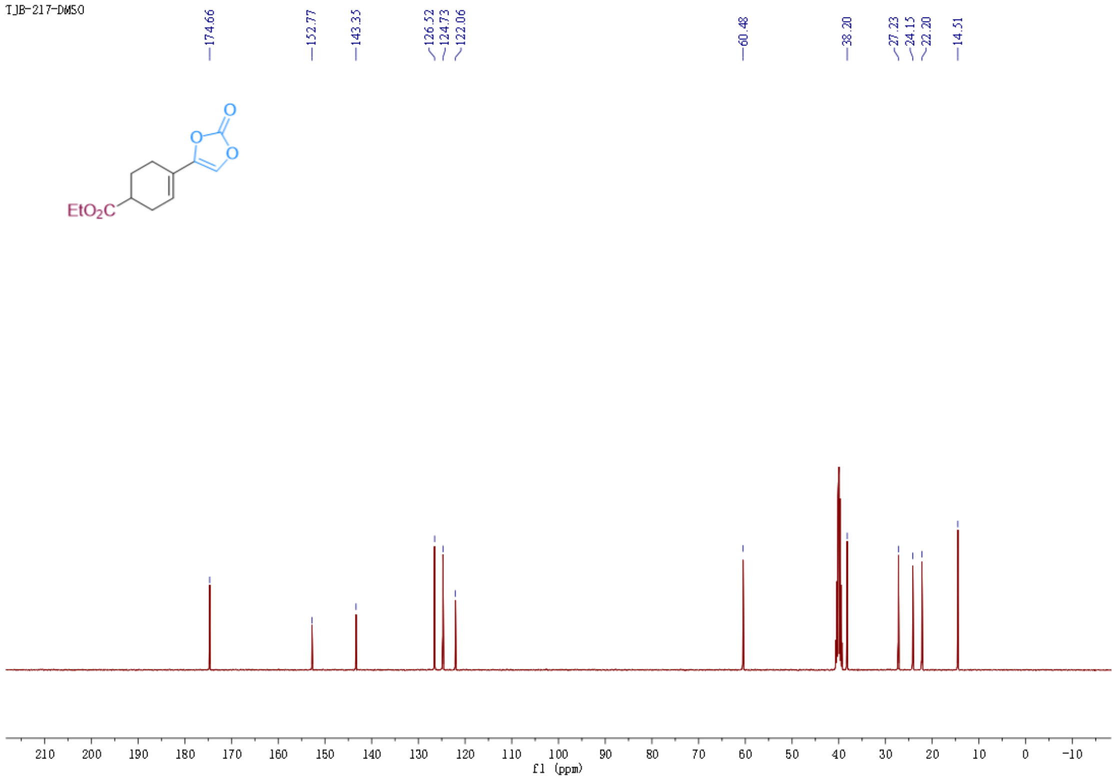
^{13}C NMR spectra of 3k (101 MHz, $(CD_3)_2SO$)



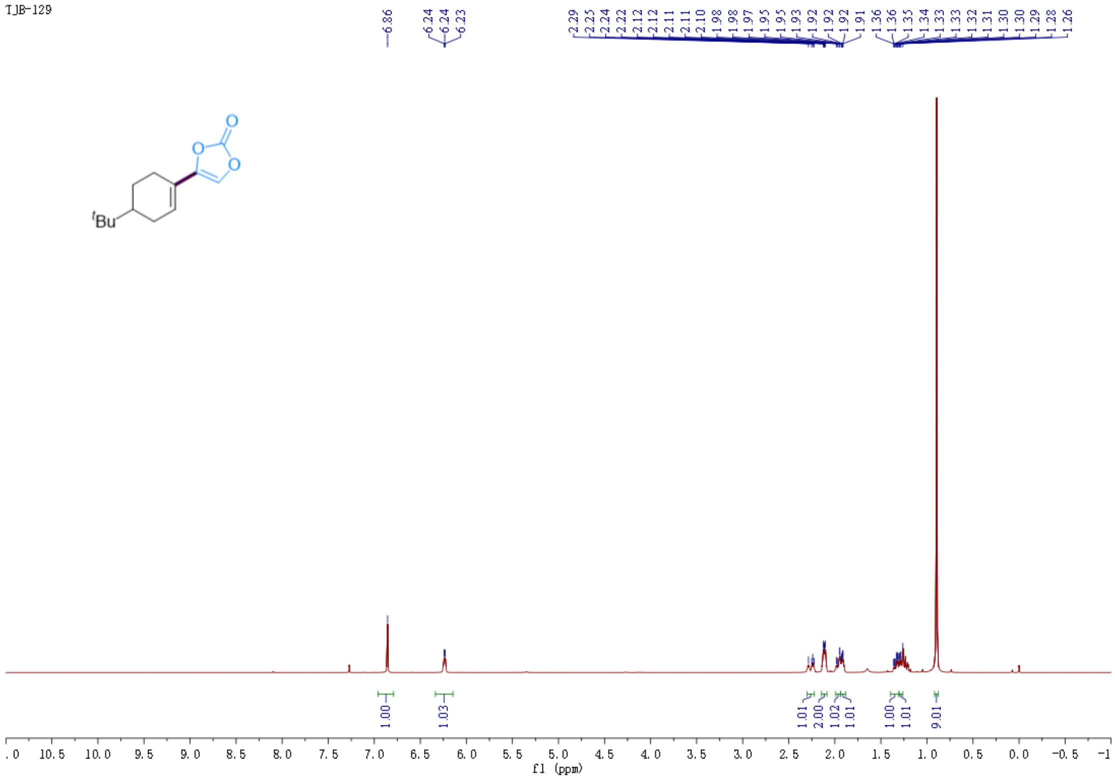
^{1}H NMR spectra of 3l (400 MHz, $(CD_3)_2SO$)



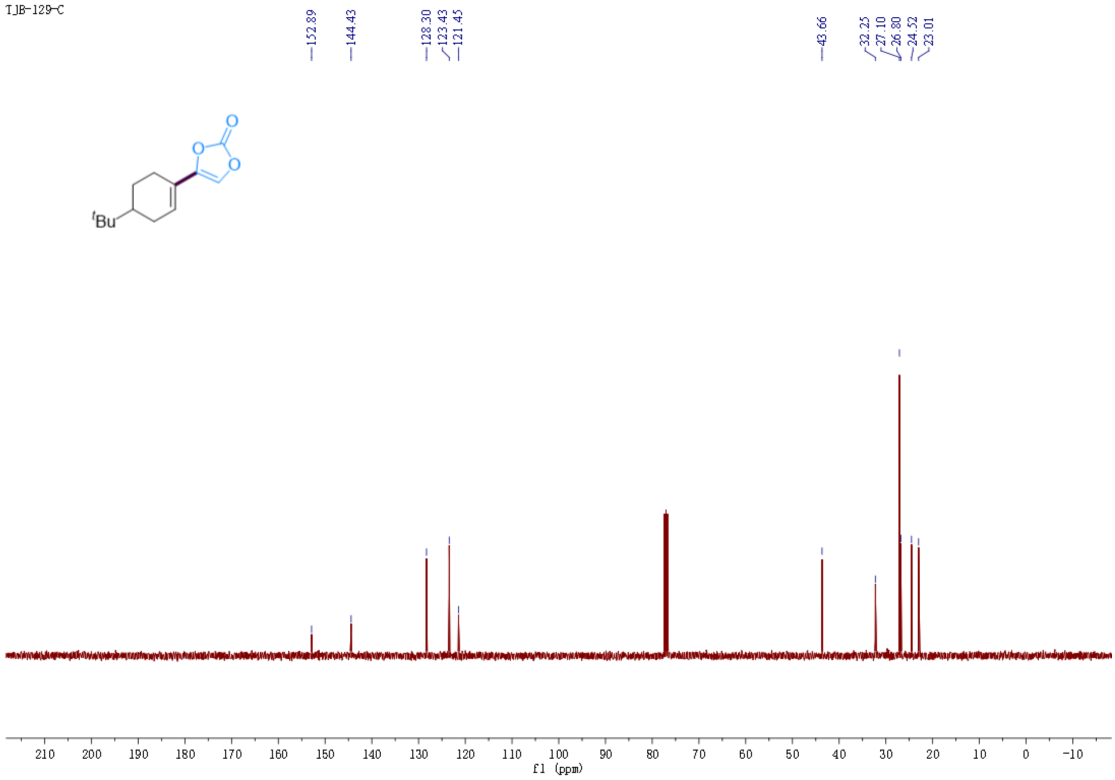
^{13}C NMR spectra of 3l (101 MHz, $(CD_3)_2SO$)



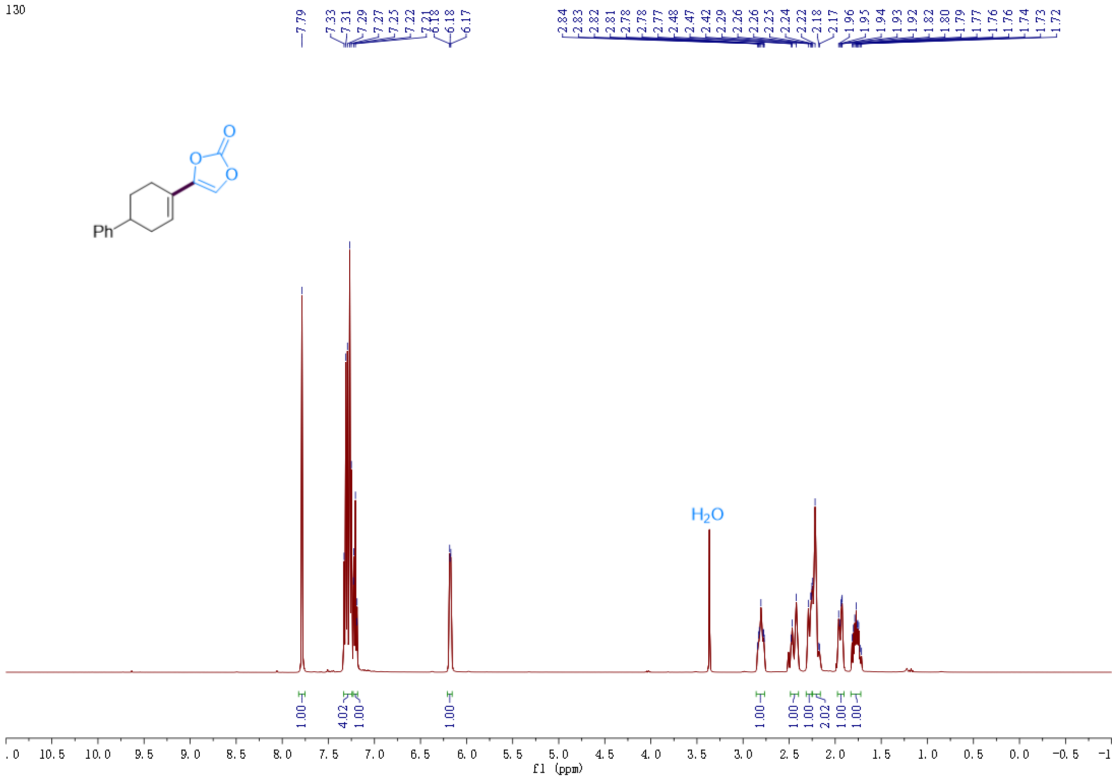
^{1}H NMR spectra of 3m (400 MHz, CDCl$_3$)



^{13}C NMR spectra of 3m (101 MHz, CDCl$_3$)



^{1}H NMR spectra of 3n (400 MHz, (CD$_3$)$_2$SO)



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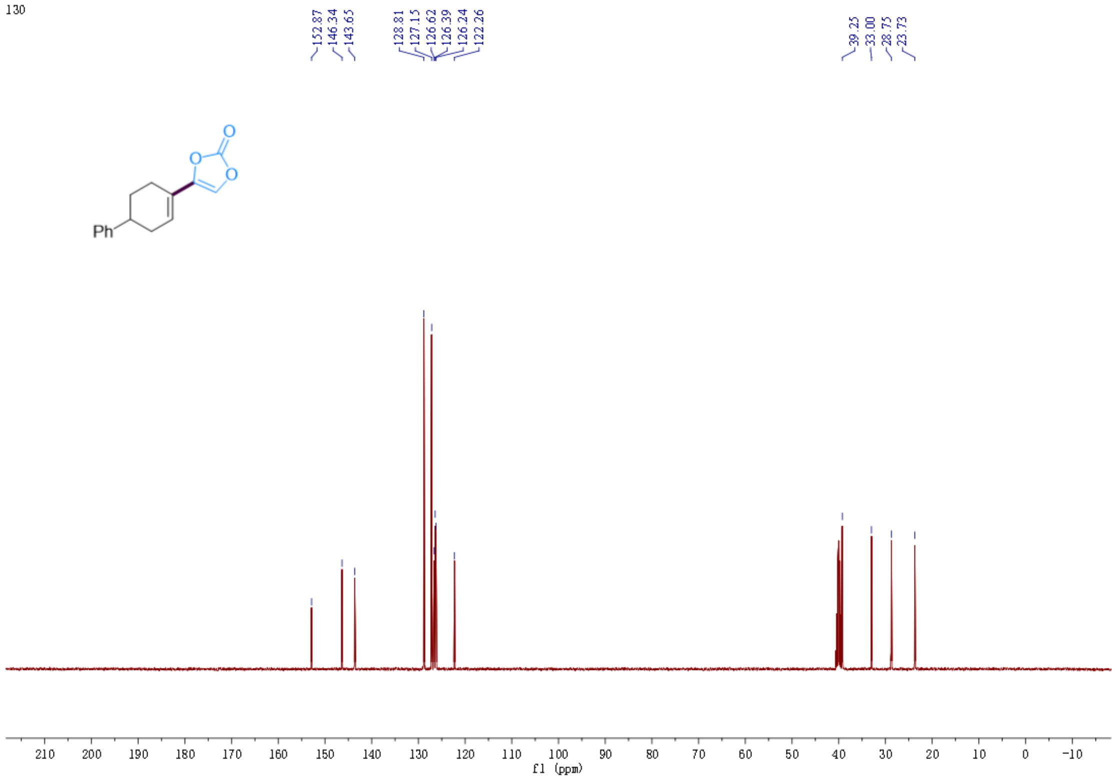

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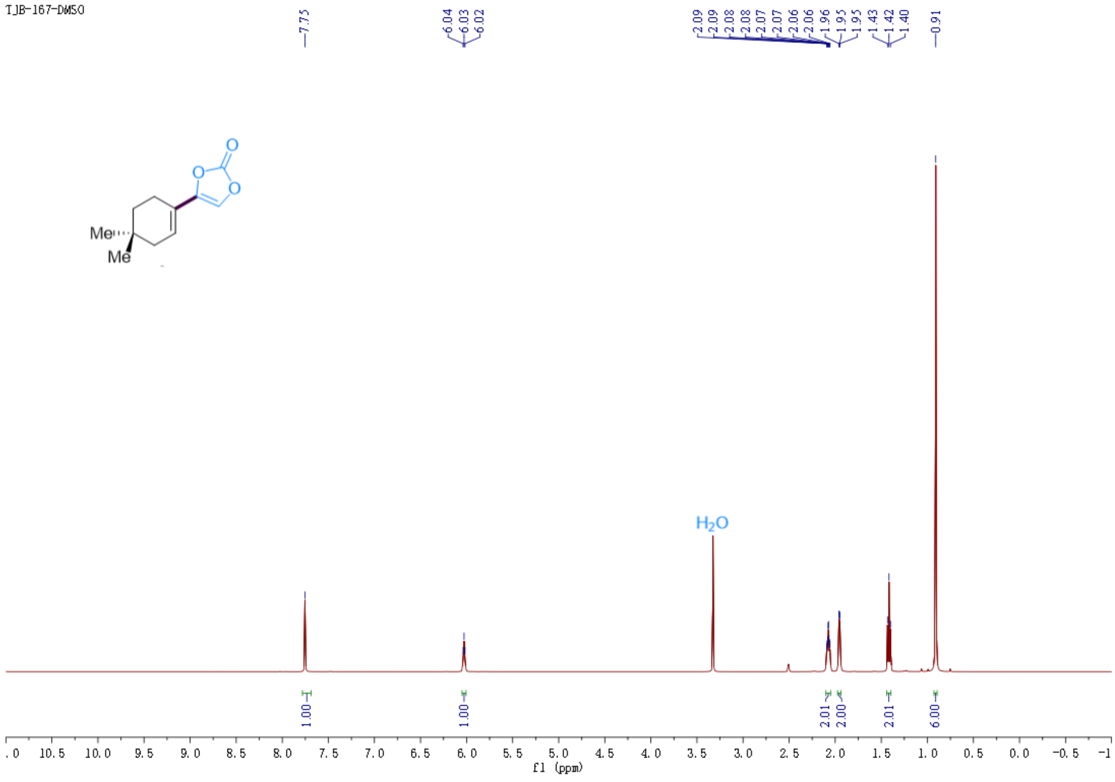

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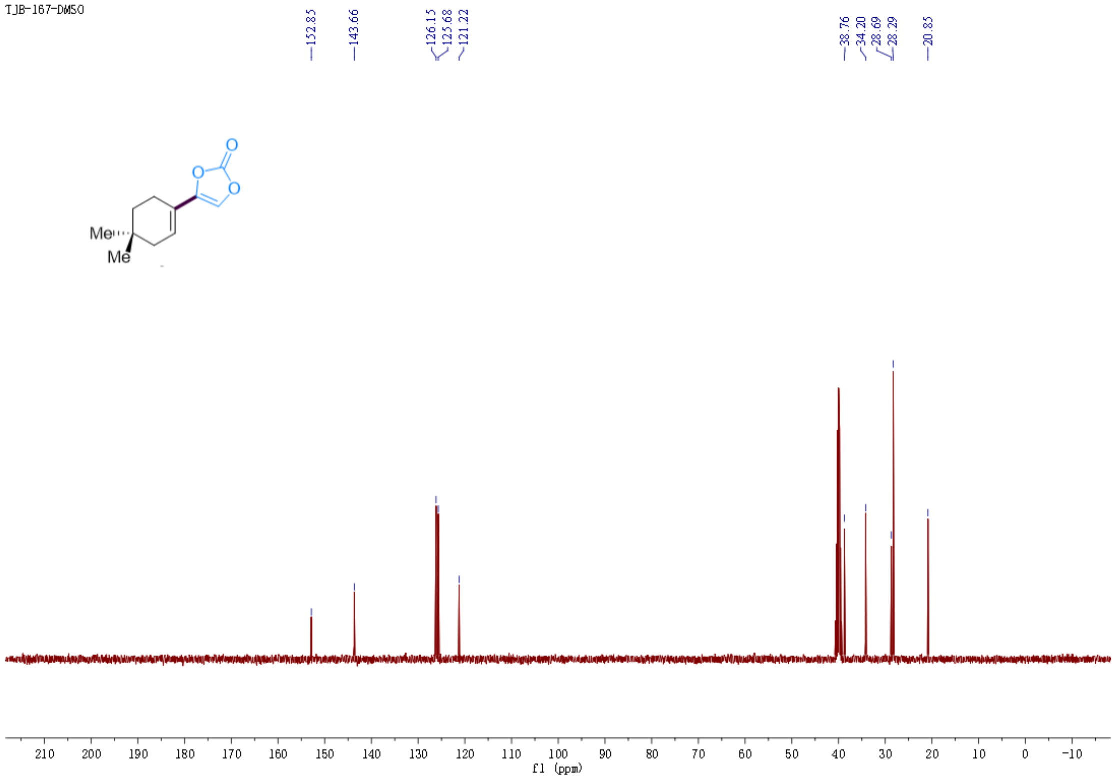
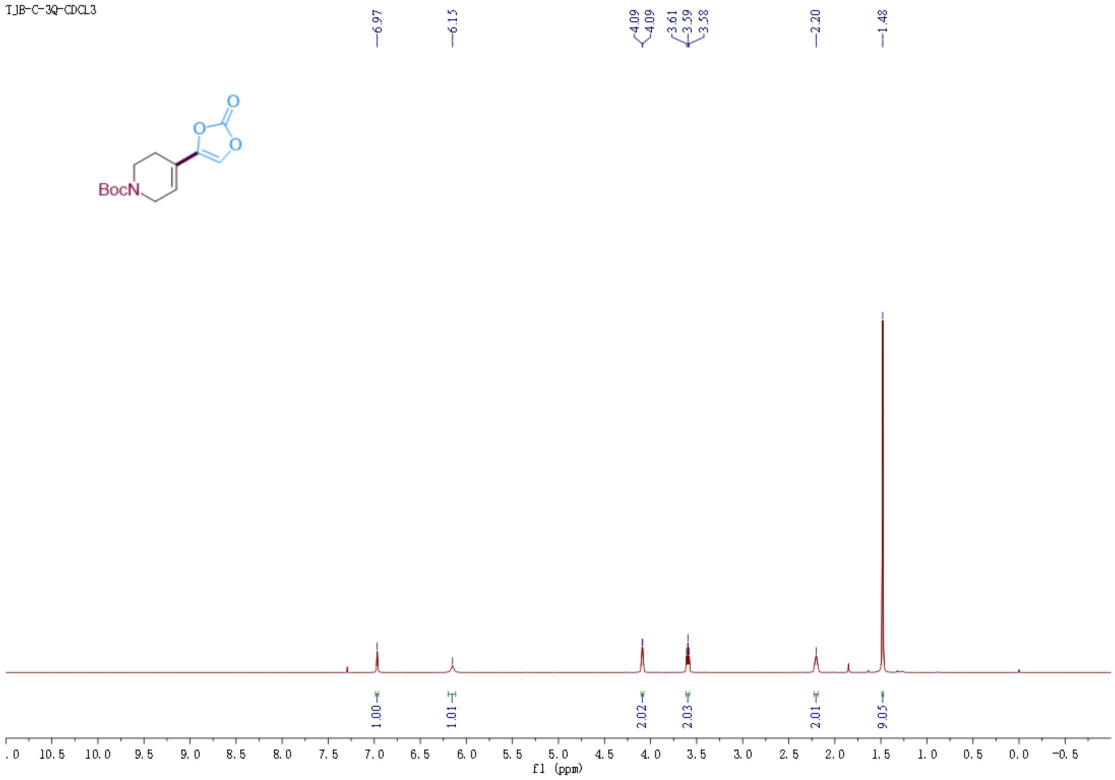
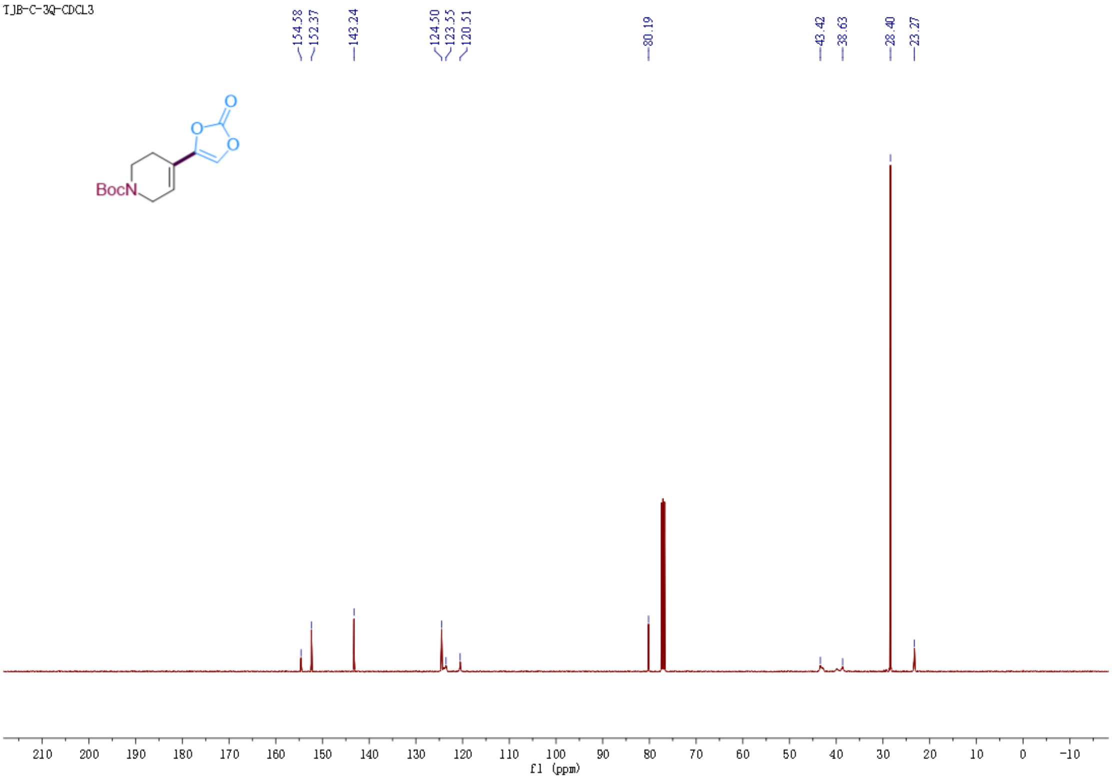


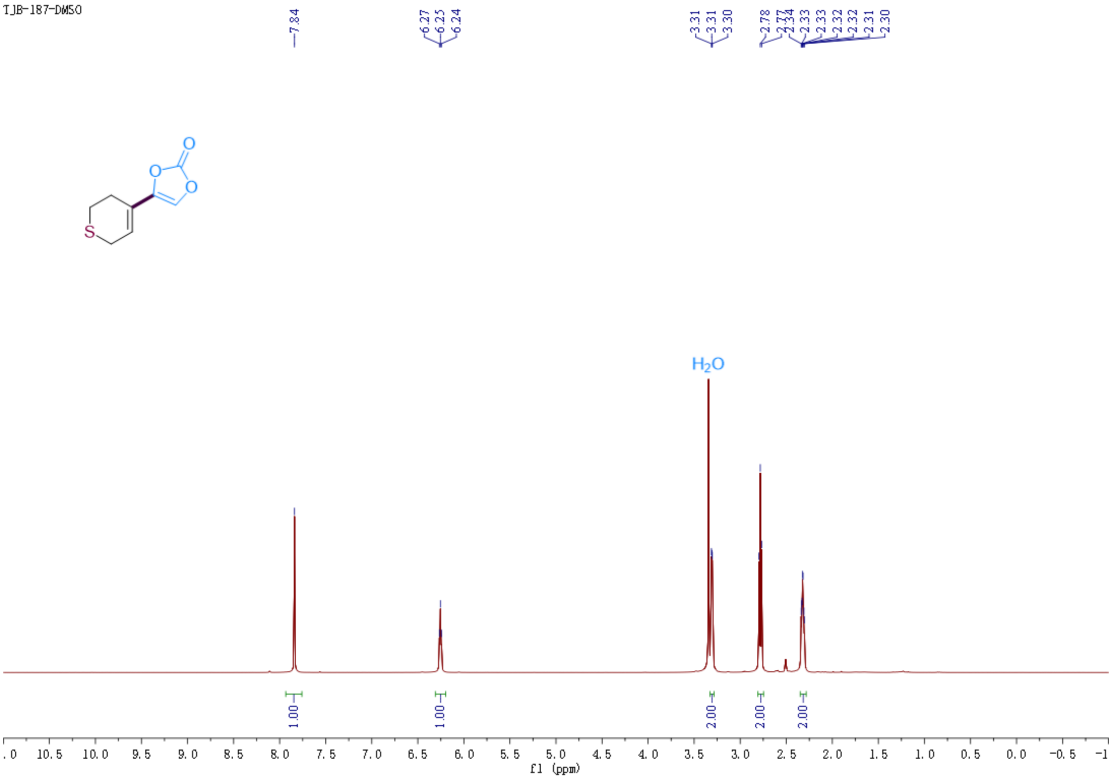
^1H NMR spectra of 3p (400 MHz, $CDCl_3$)



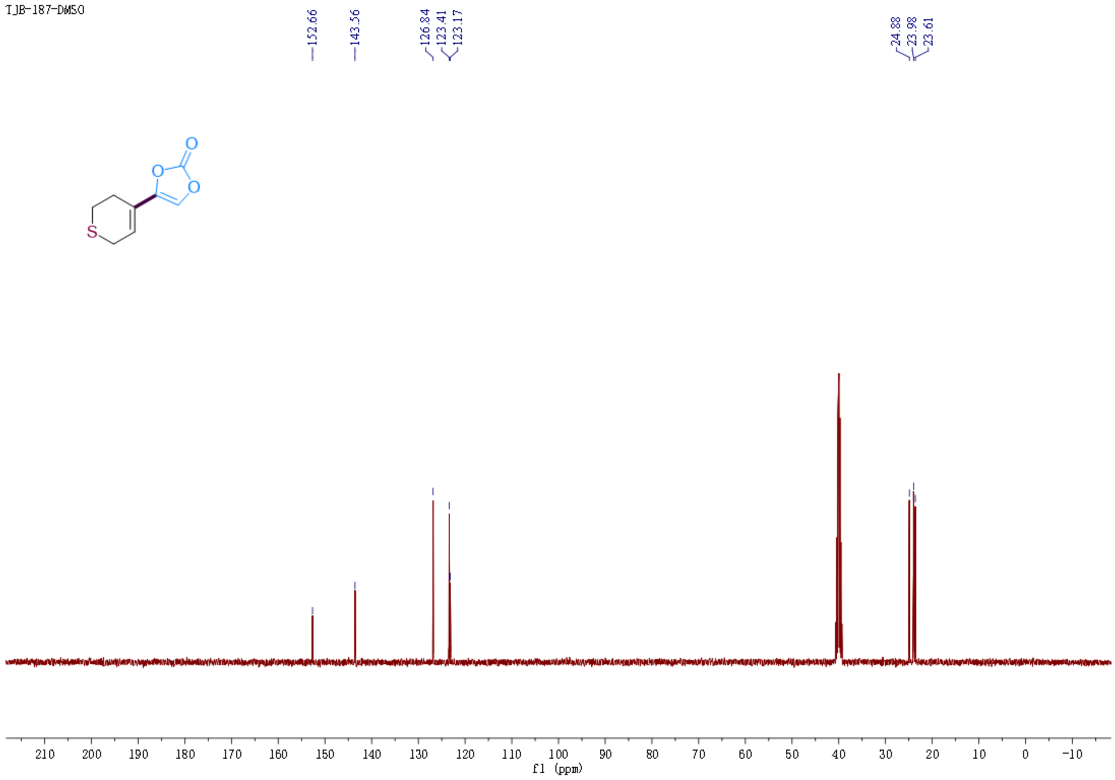
^{13}C NMR spectra of 3p (101 MHz, $CDCl_3$)



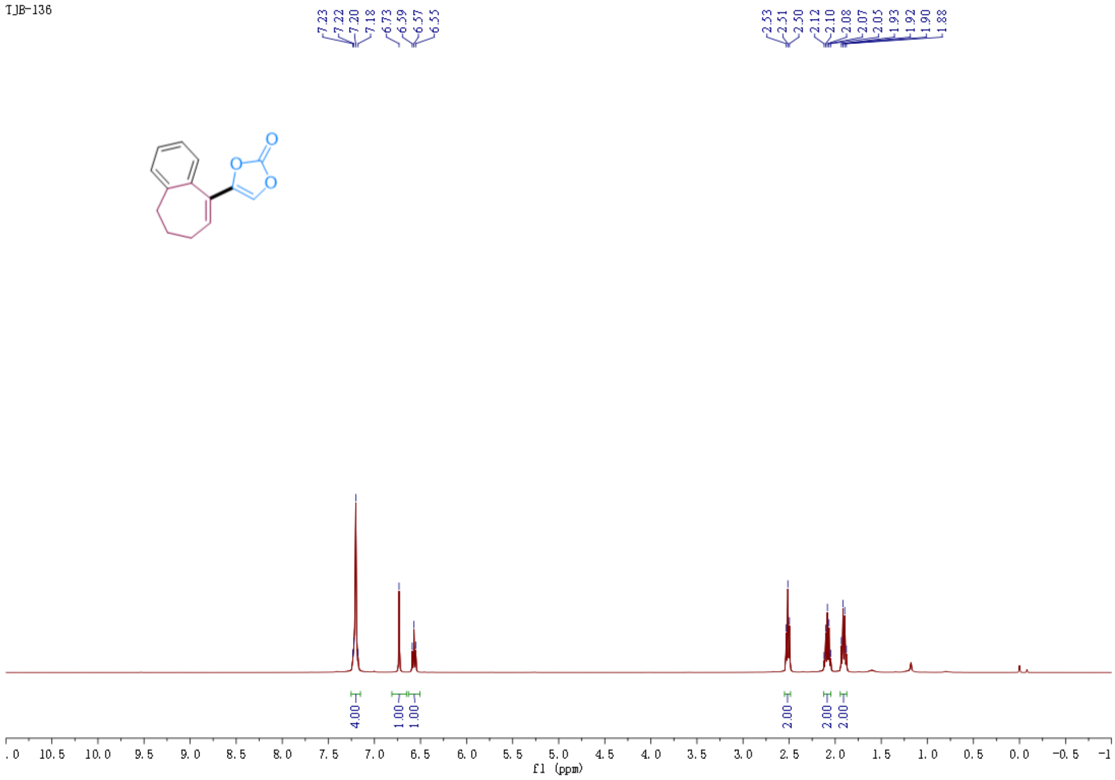
^1H NMR spectra of 3q (400 MHz, $(CD_3)_2SO$)



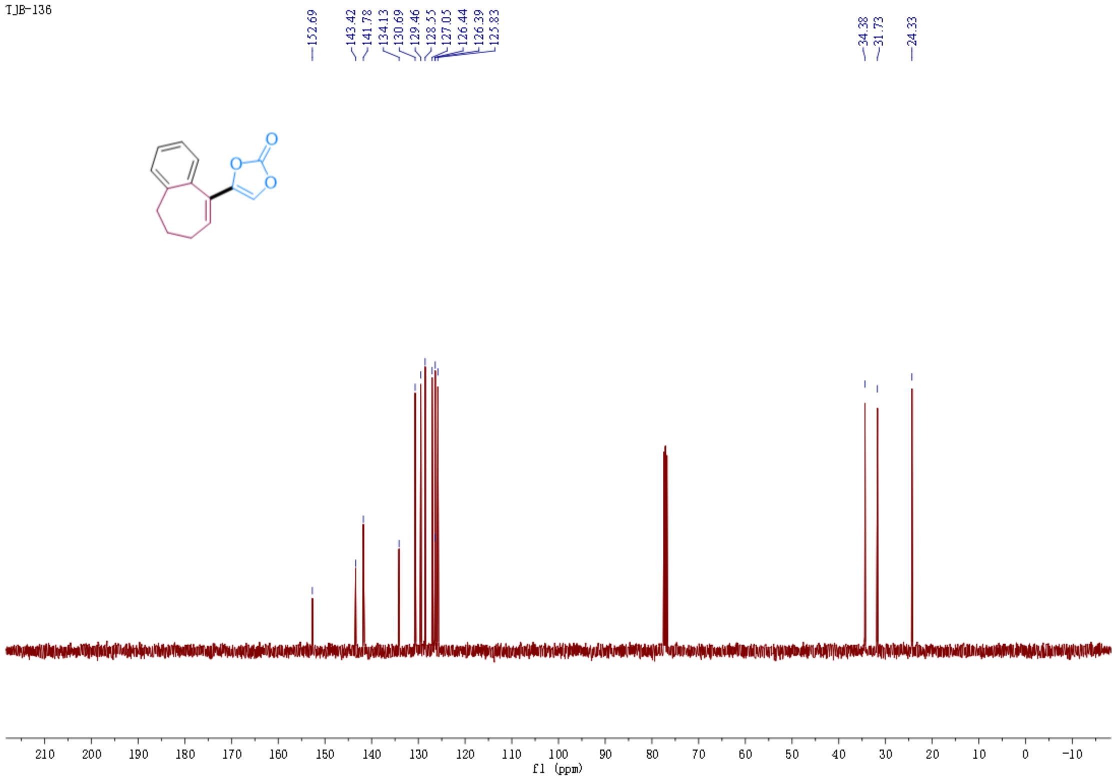
^{13}C NMR spectra of 3q (101 MHz, $(CD_3)_2SO$)



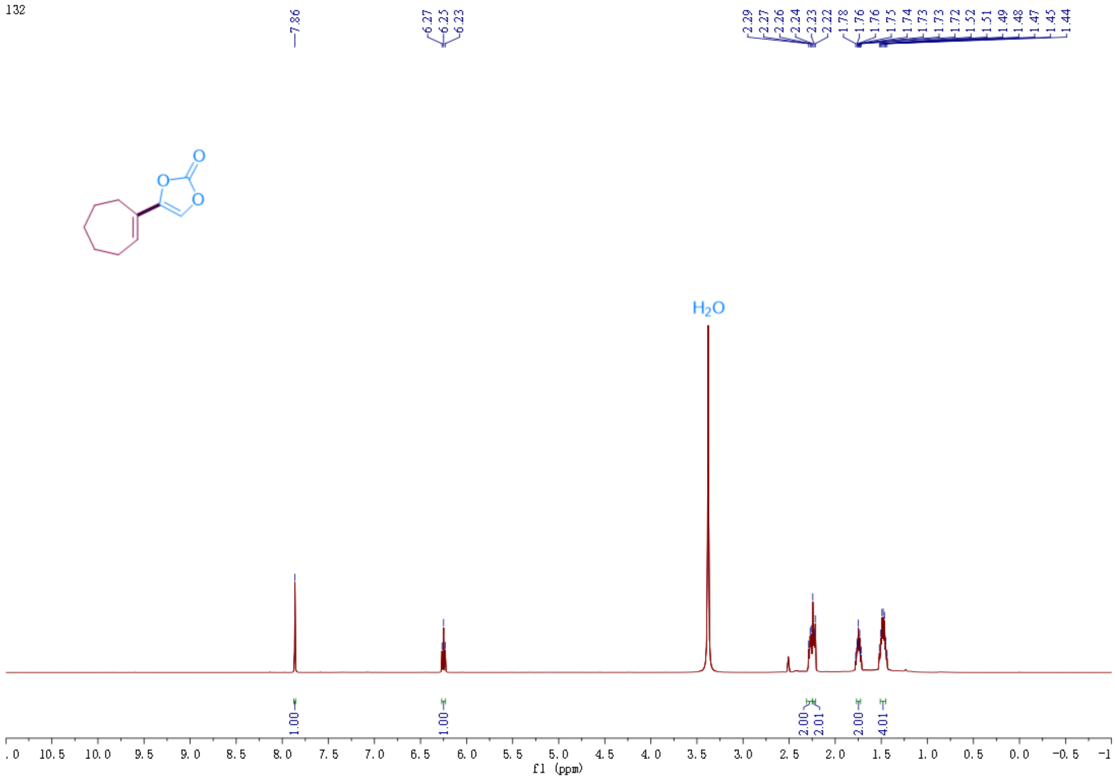
^{1}H NMR spectra of 3r (400 MHz, $CDCl_3$)



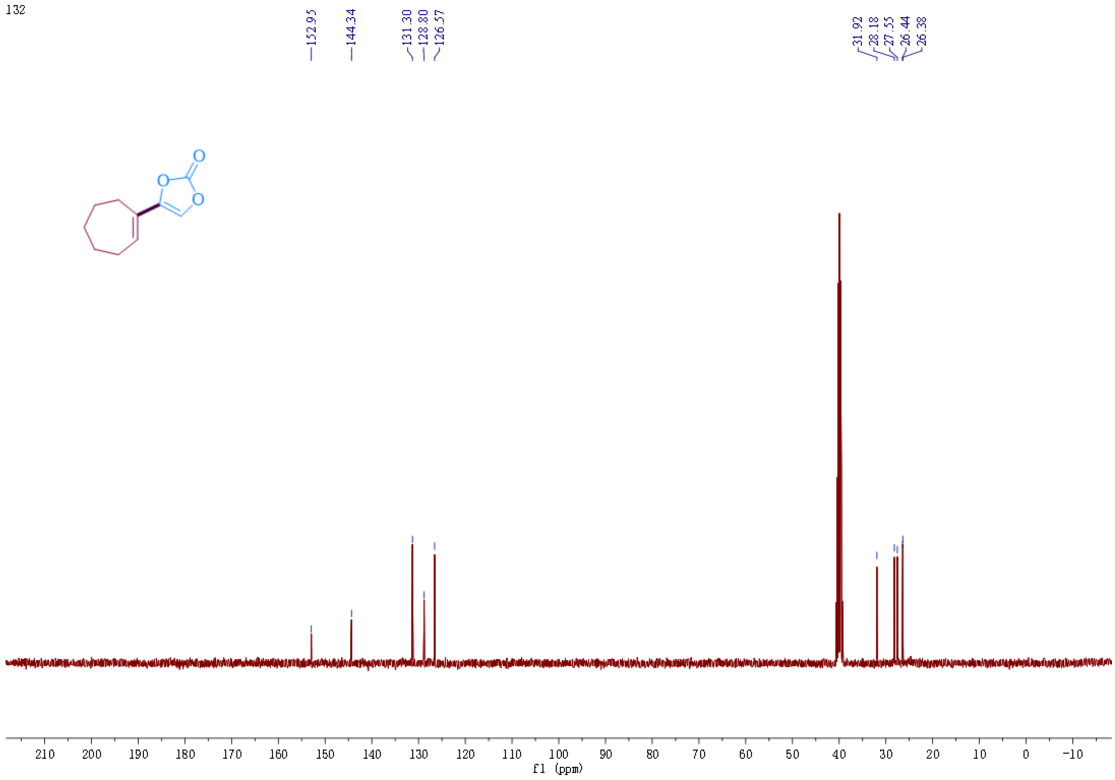
^{13}C NMR spectra of 3r (101 MHz, $CDCl_3$)



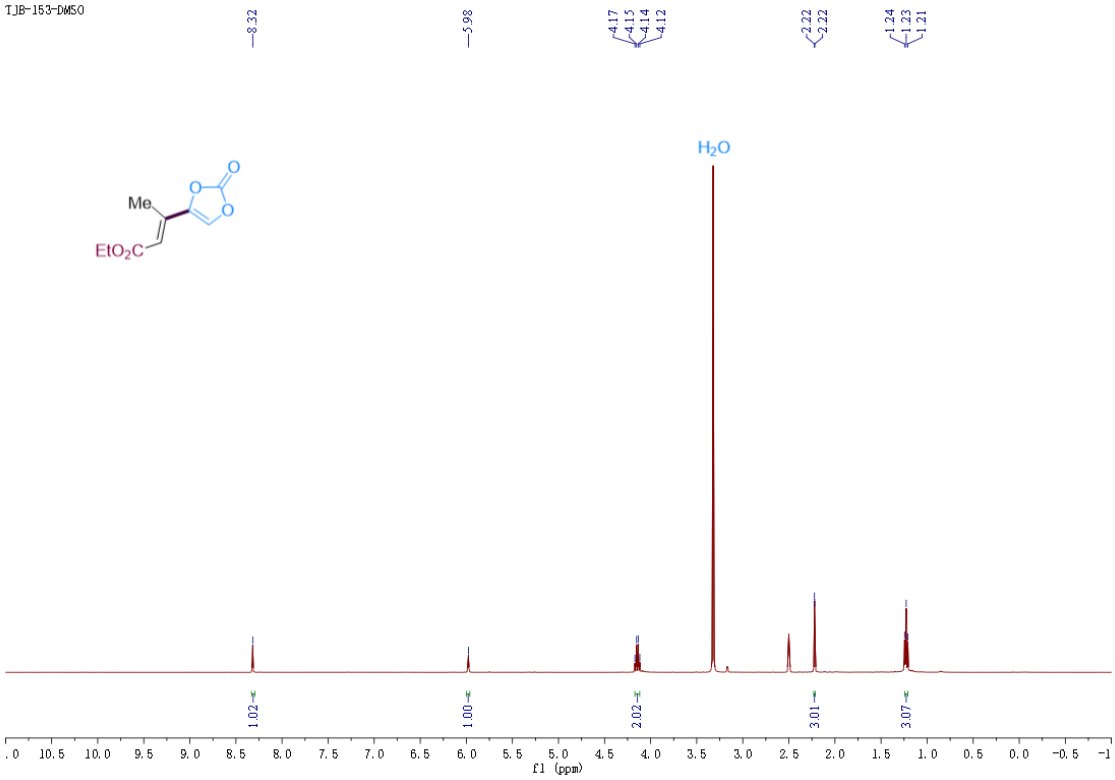
^{1}H NMR spectra of 3s (400 MHz, $(CD_3)_2SO$)



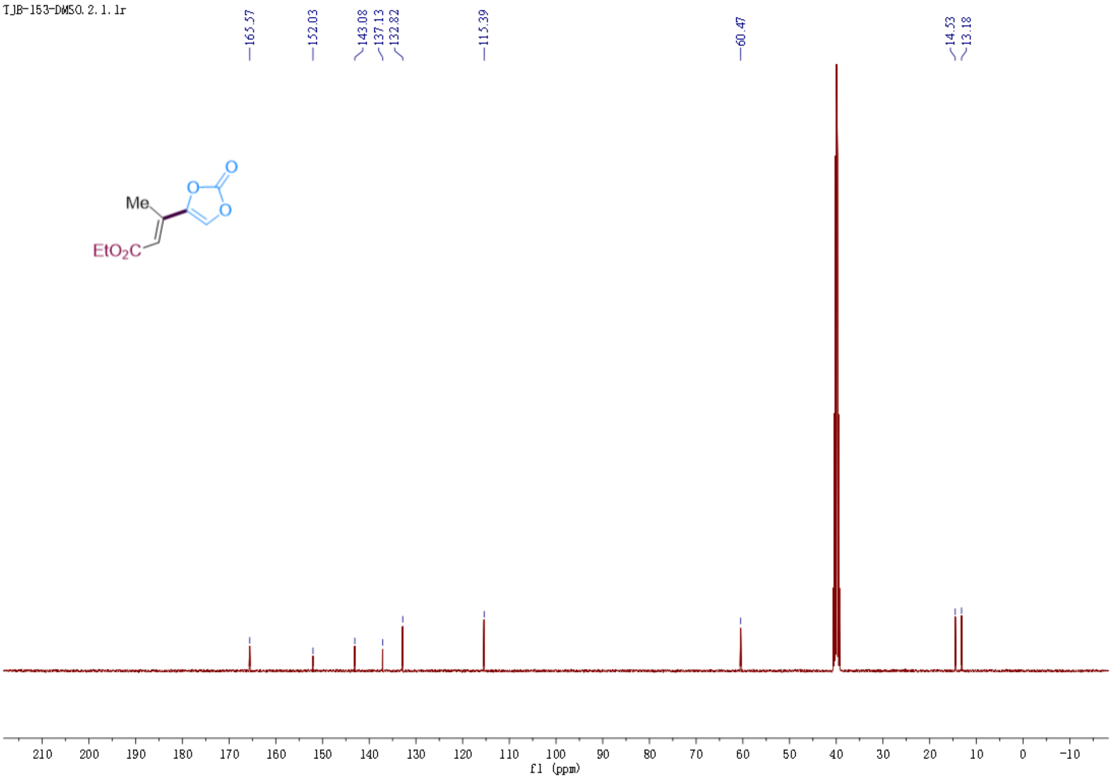
^{13}C NMR spectra of 3s (101 MHz, $(CD_3)_2SO$)



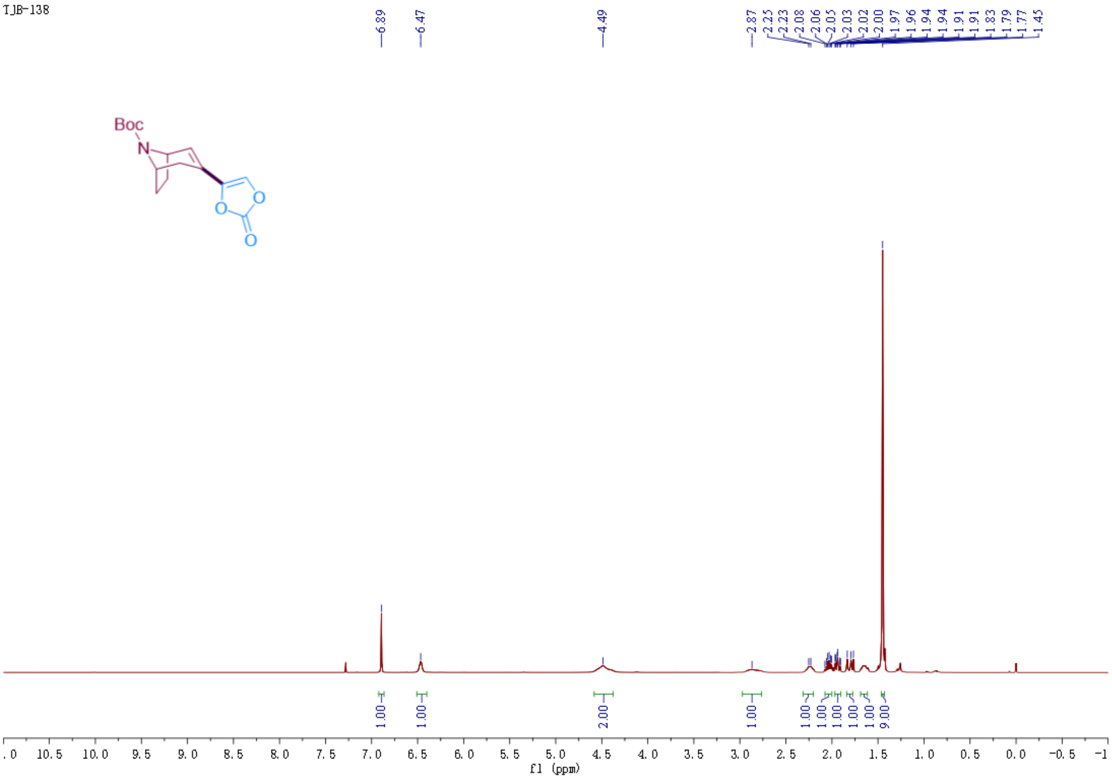
^{1}H NMR spectra of 3t (400 MHz, $(CD_3)_2SO$)



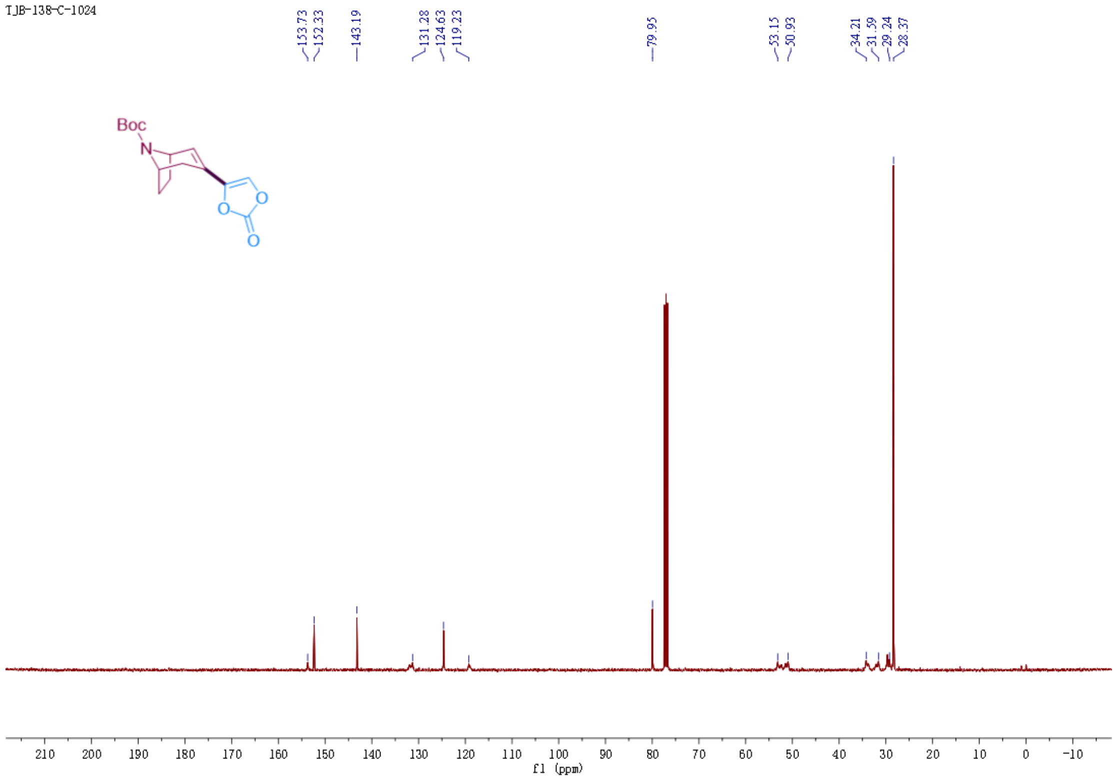
^{13}C NMR spectra of 3t (101 MHz, $(CD_3)_2SO$)



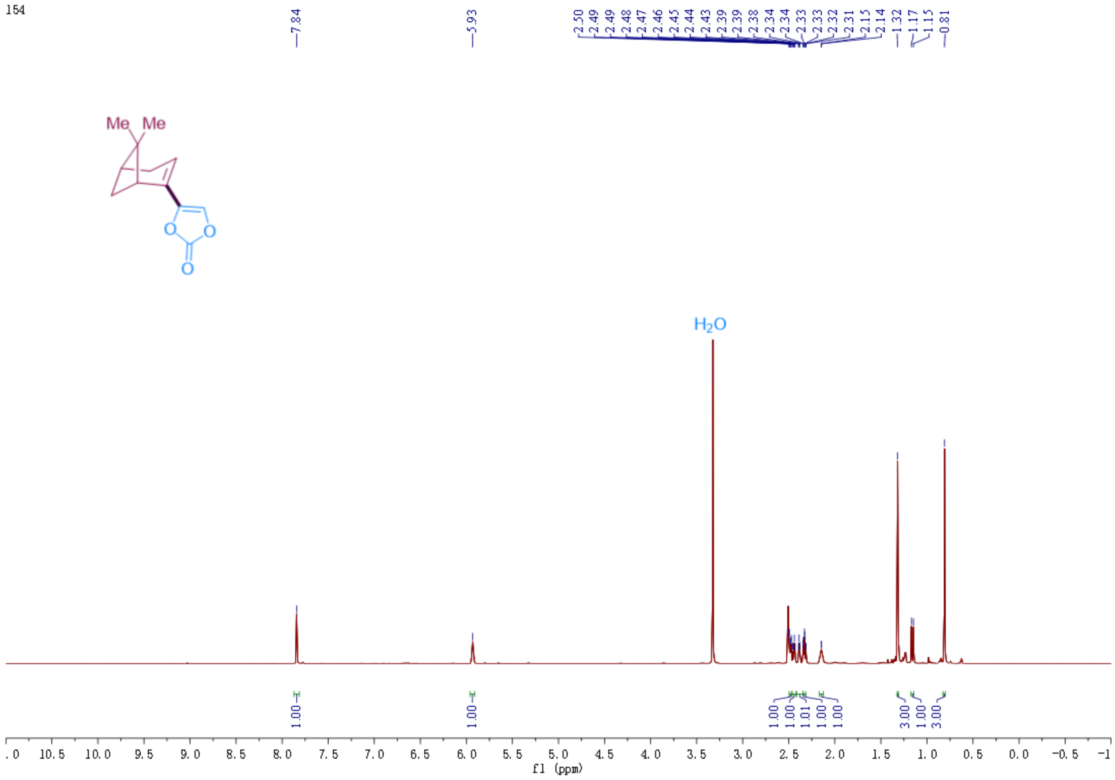
^{1}H NMR spectra of 3u (400 MHz, $CDCl_3$)



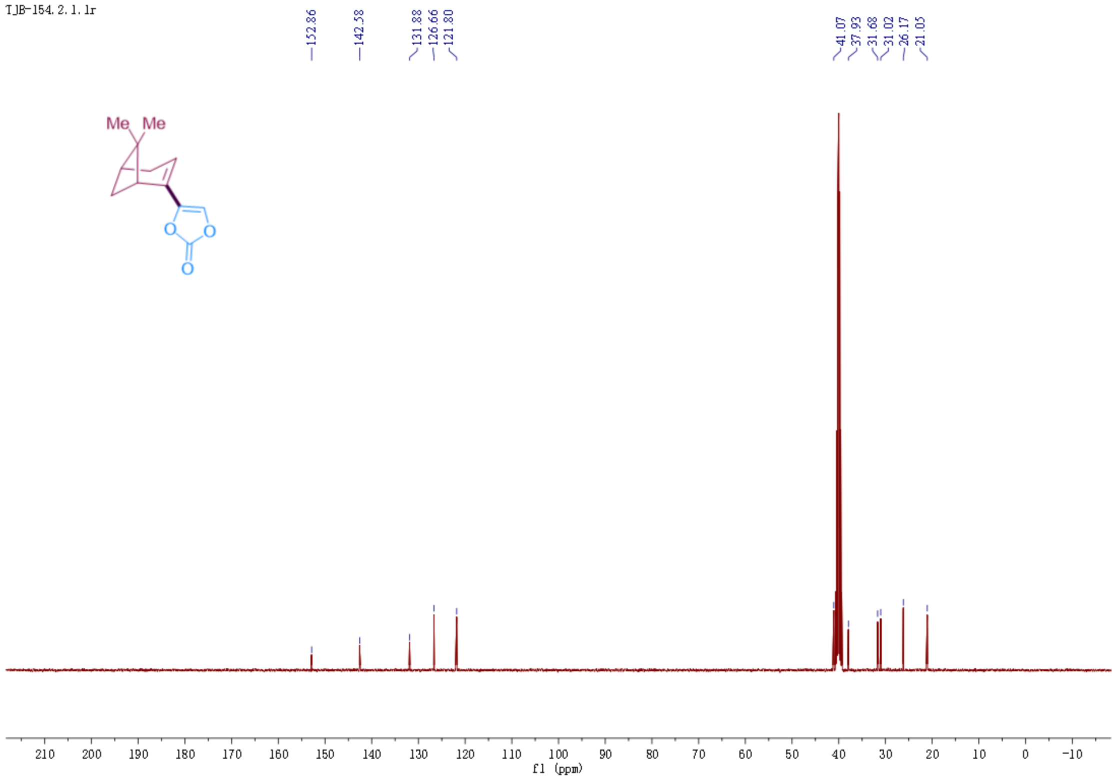
^{13}C NMR spectra of 3u (101 MHz, CDCl$_3$)



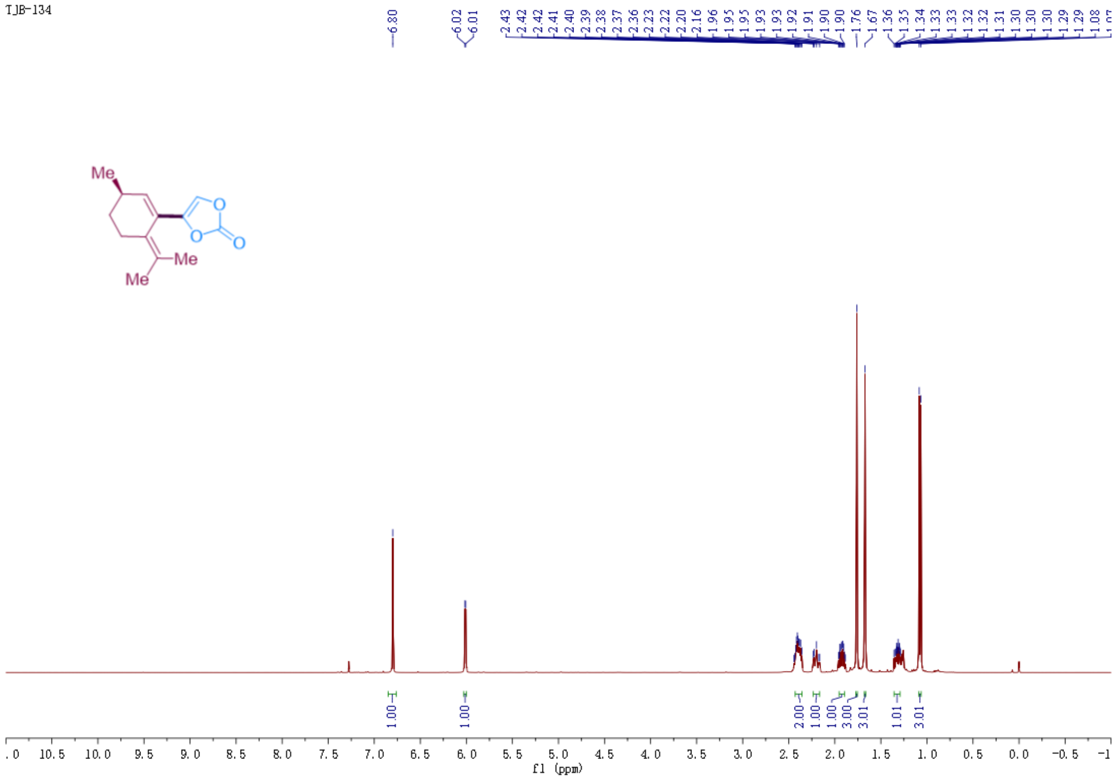
^{1}H NMR spectra of 3v (400 MHz, (CD$_3$)$_2$SO)



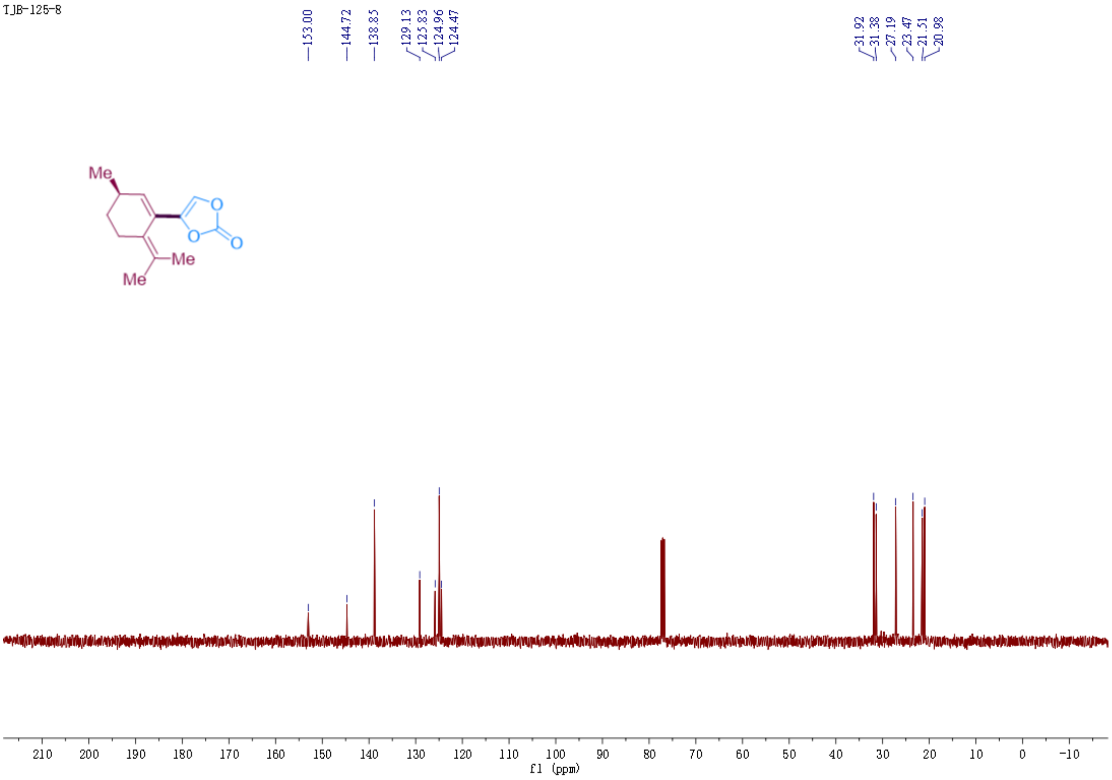
^{13}C NMR spectra of 3v (101 MHz, $(CD_3)_2SO$)



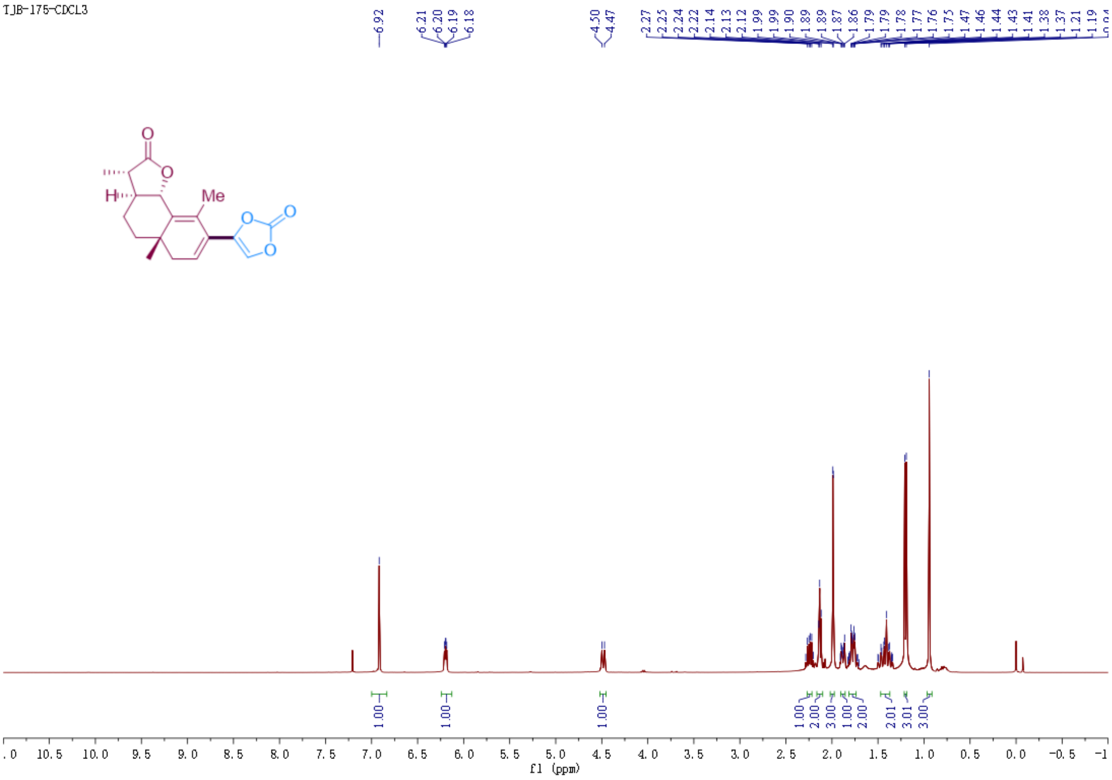
^{1}H NMR spectra of 3w (400 MHz, $CDCl_3$)



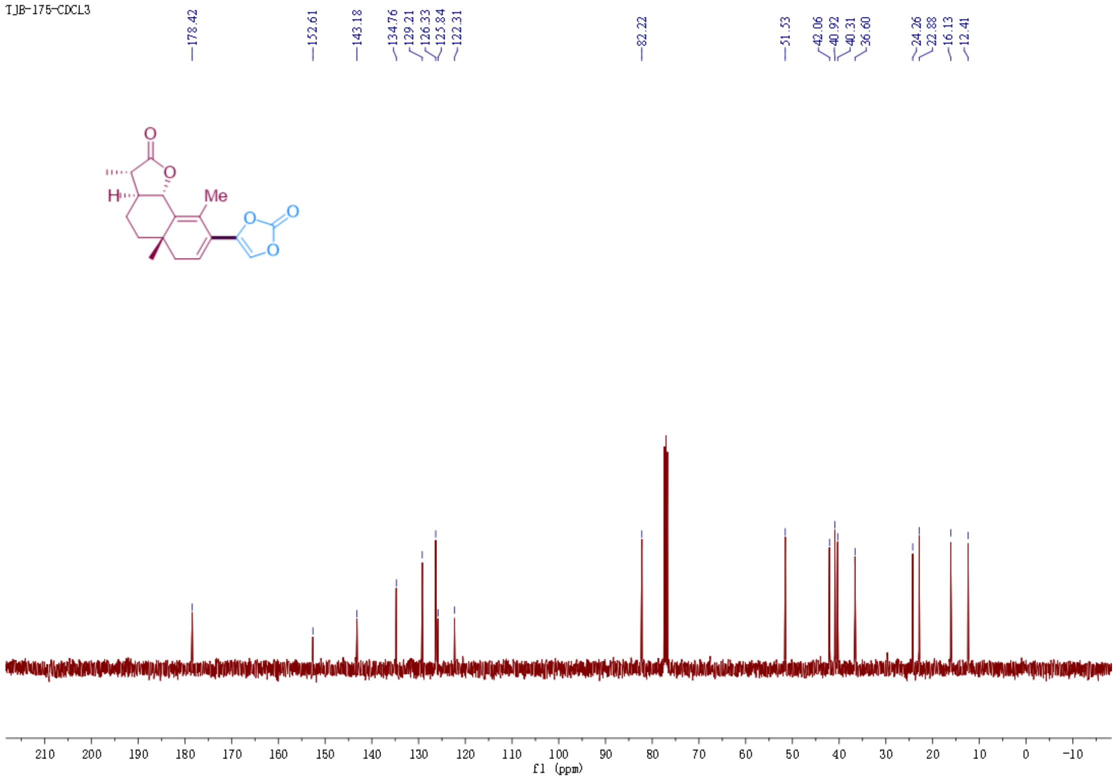
^{13}C NMR spectra of 3w (101 MHz, CDCl$_3$)



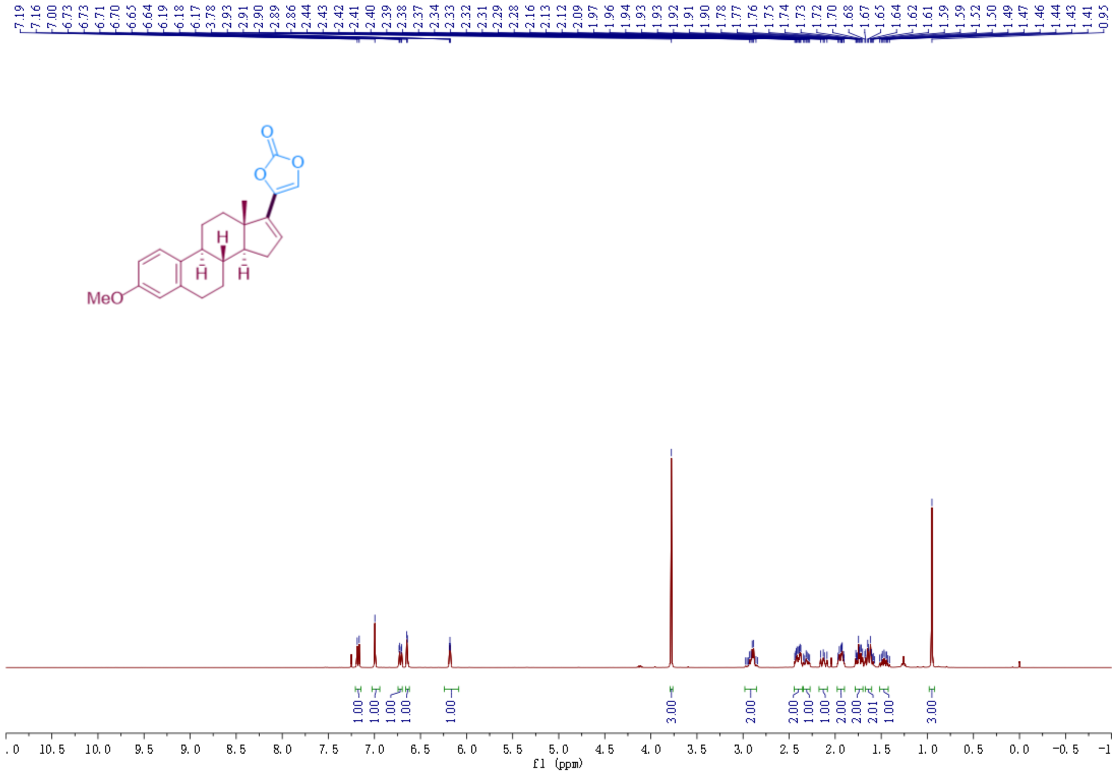
^{1}H NMR spectra of 3x (400 MHz, CDCl$_3$)



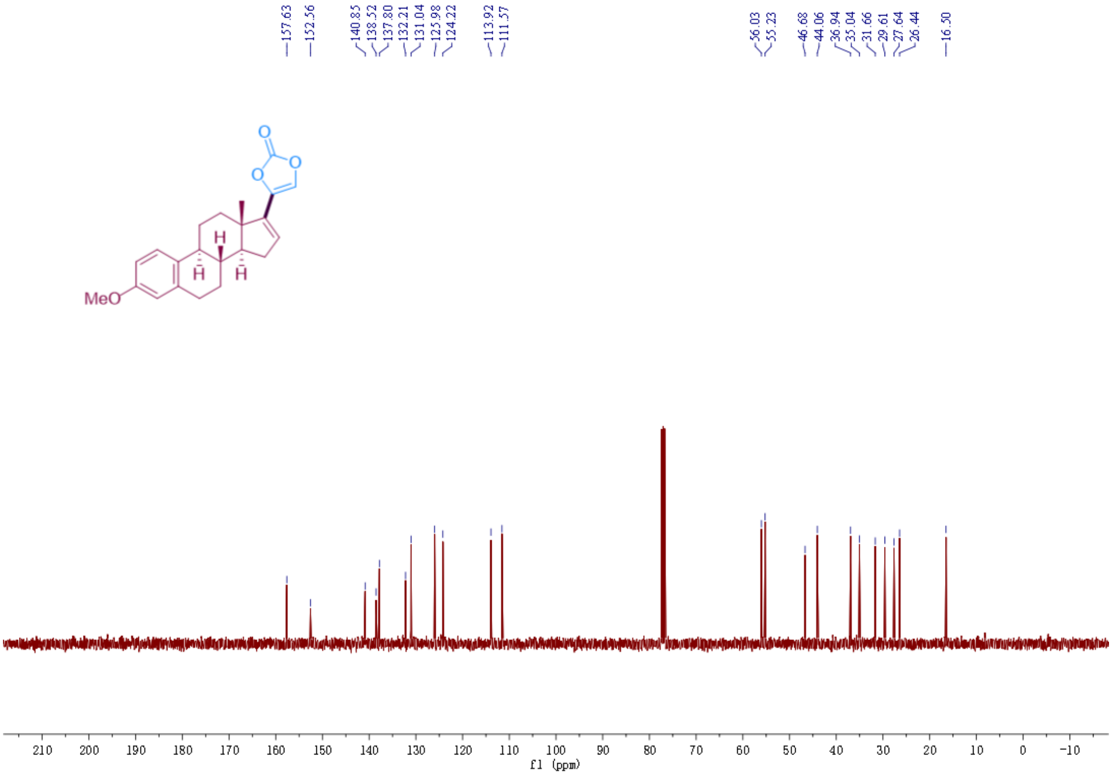
^{13}C NMR spectra of 3x (101 MHz, CDCl$_3$)



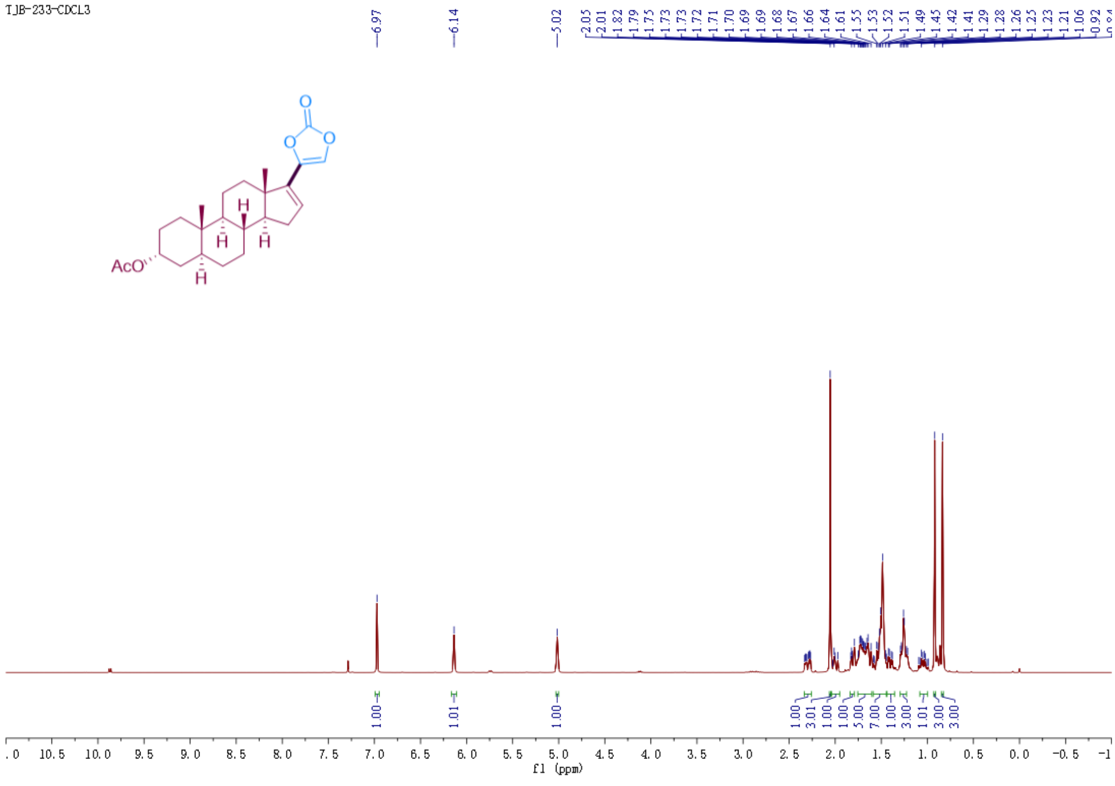
^{1}H NMR spectra of 3y (400 MHz, CDCl$_3$)



^{13}C NMR spectra of 3y (101 MHz, CDCl$_3$)



^{1}H NMR spectra of 3z (400 MHz, CDCl$_3$)



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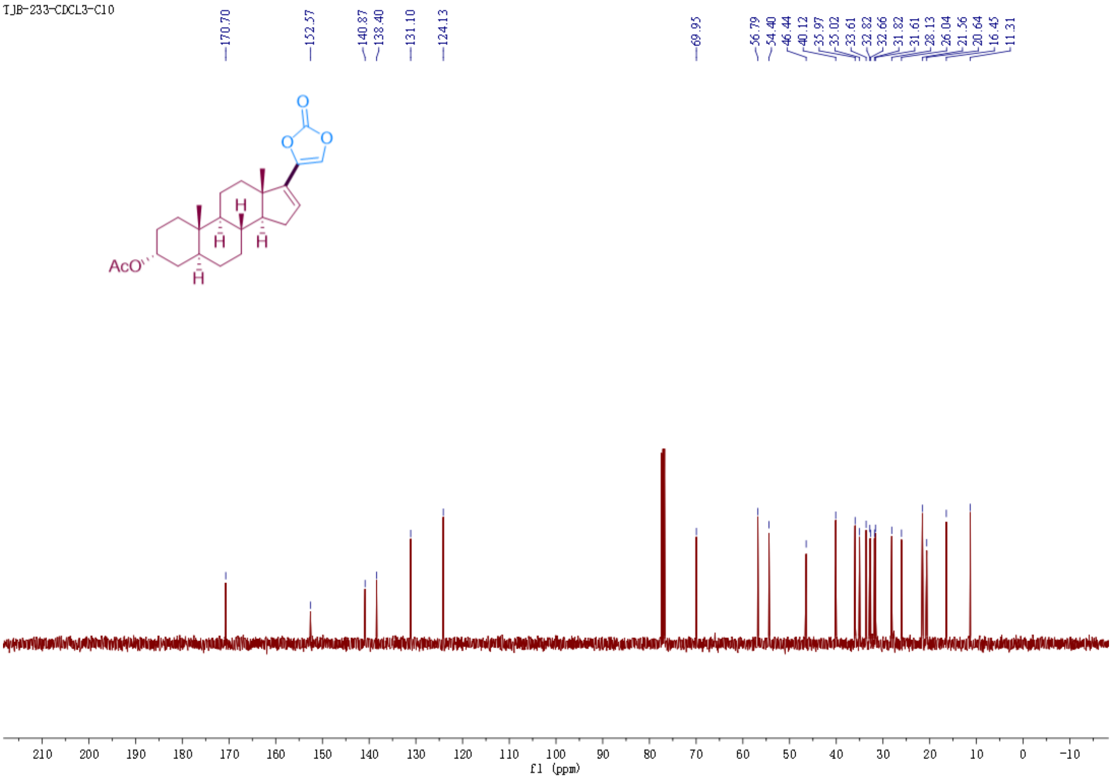
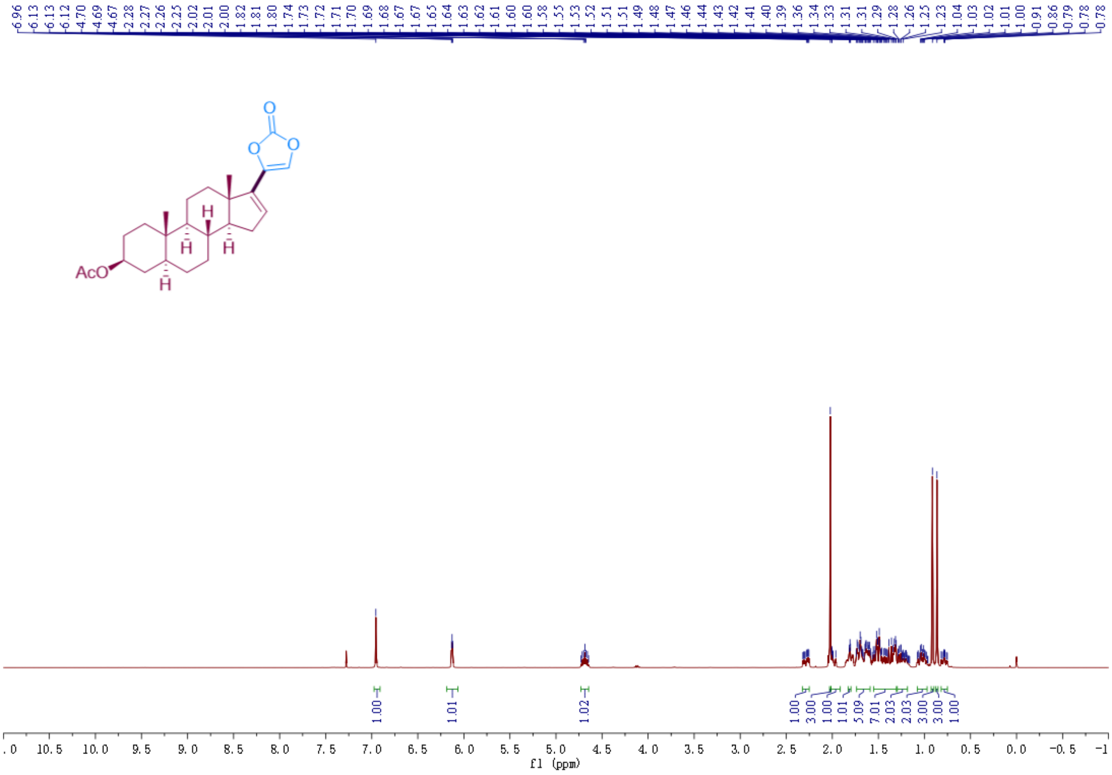
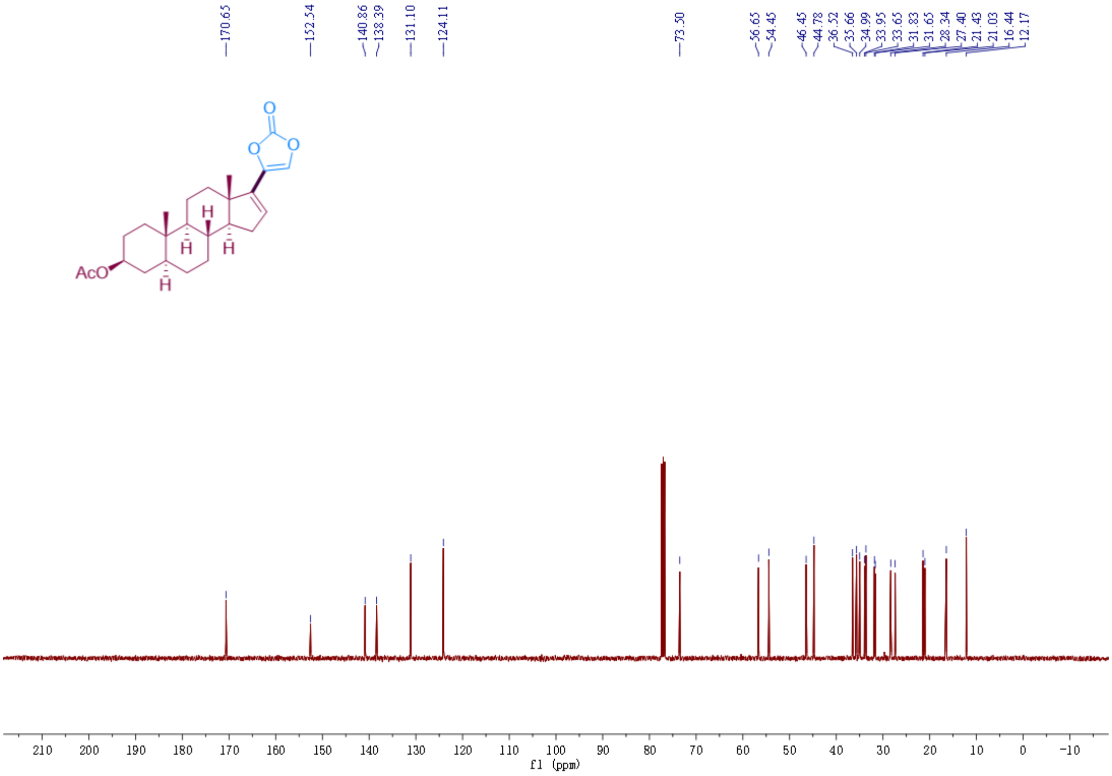


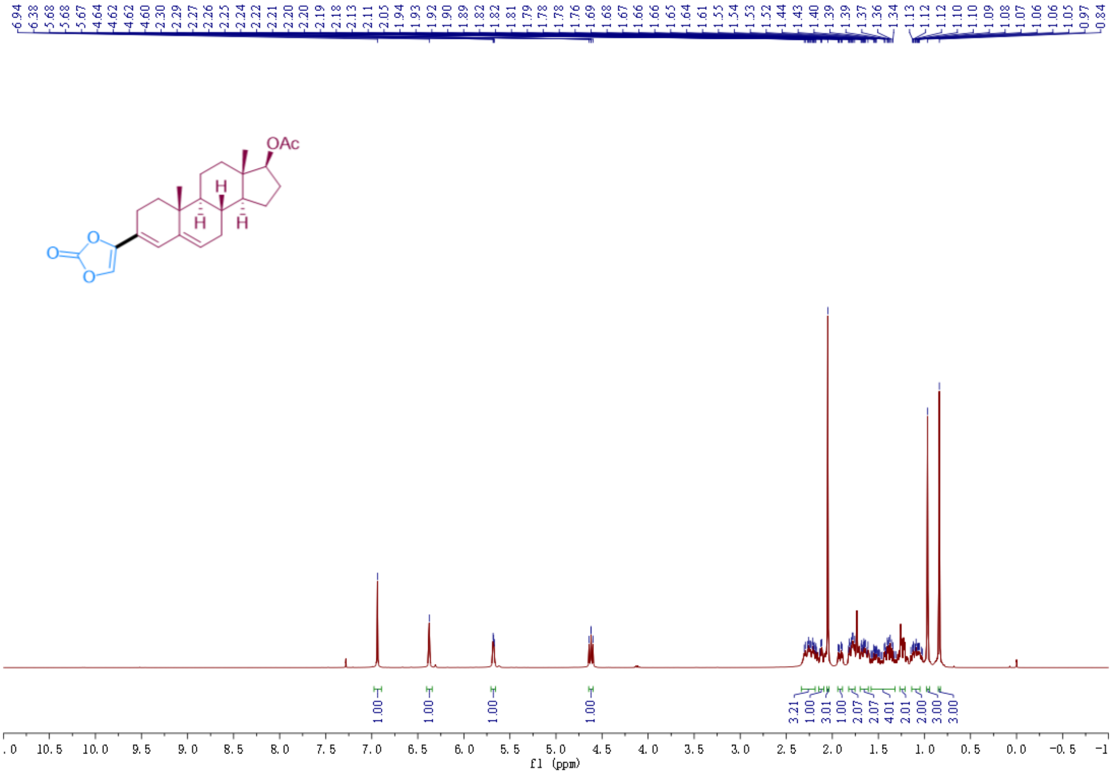
^{1}H NMR spectra of 3aa (400 MHz, CDCl$_3$)



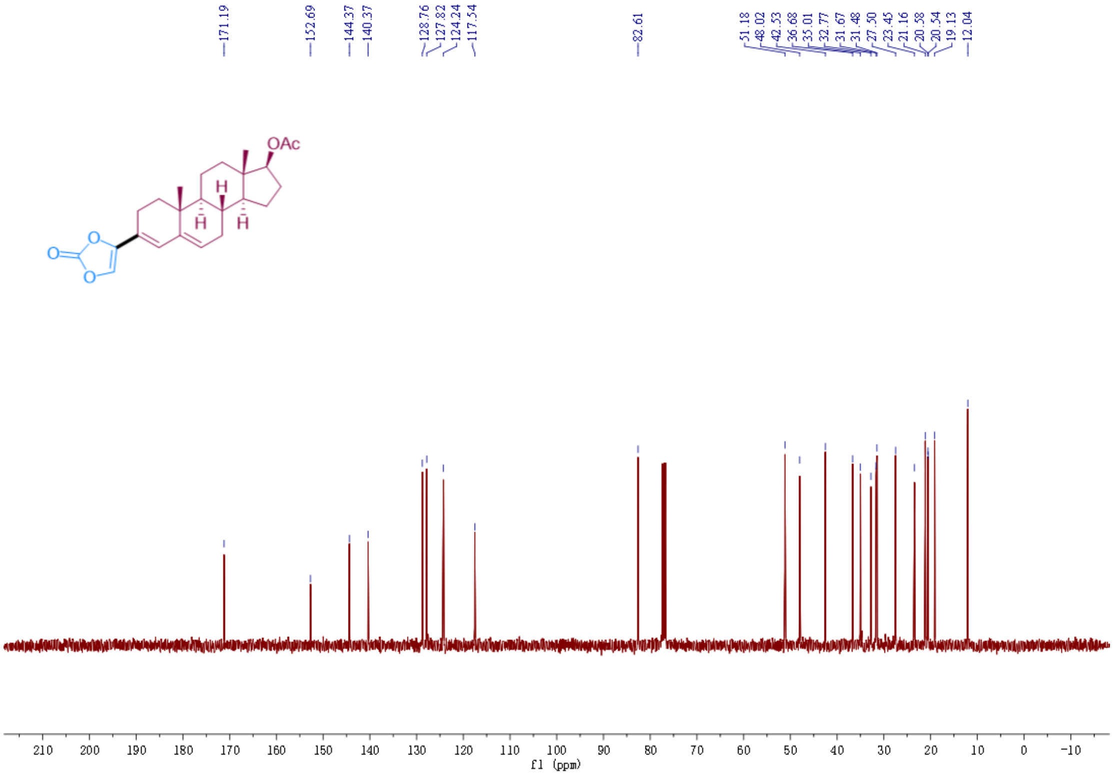
^{13}C NMR spectra of 3aa (101 MHz, CDCl$_3$)



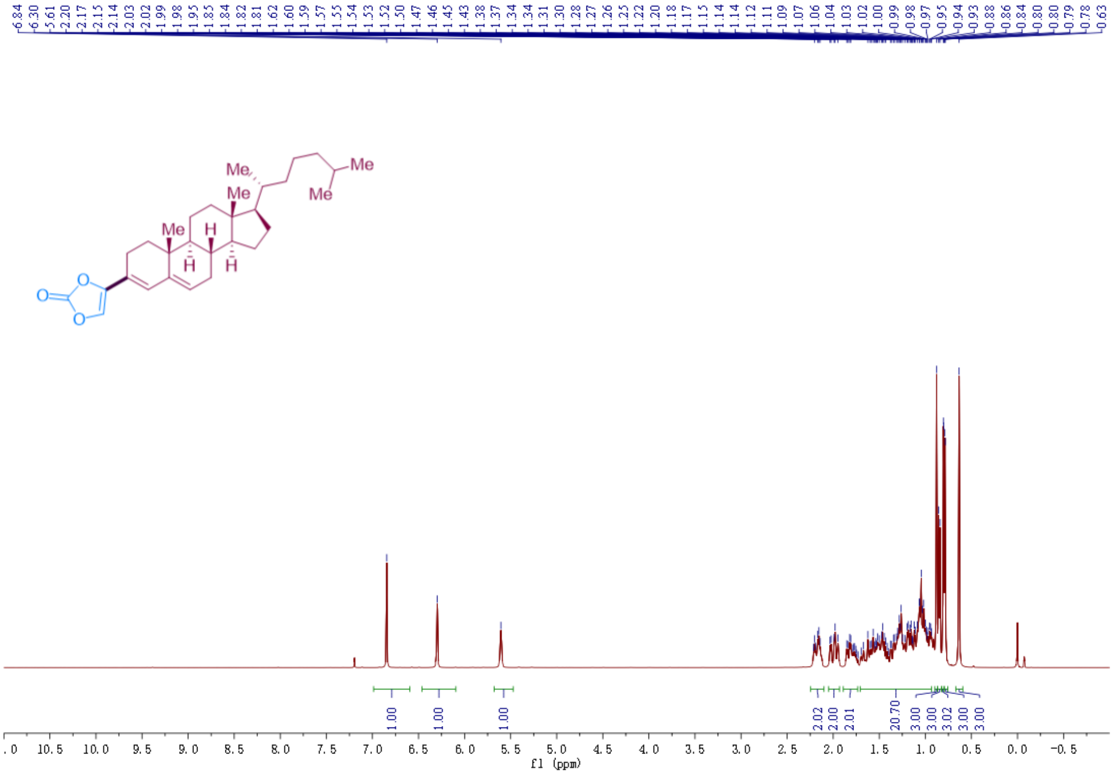
^{1}H NMR spectra of 3ab (400 MHz, CDCl$_3$)



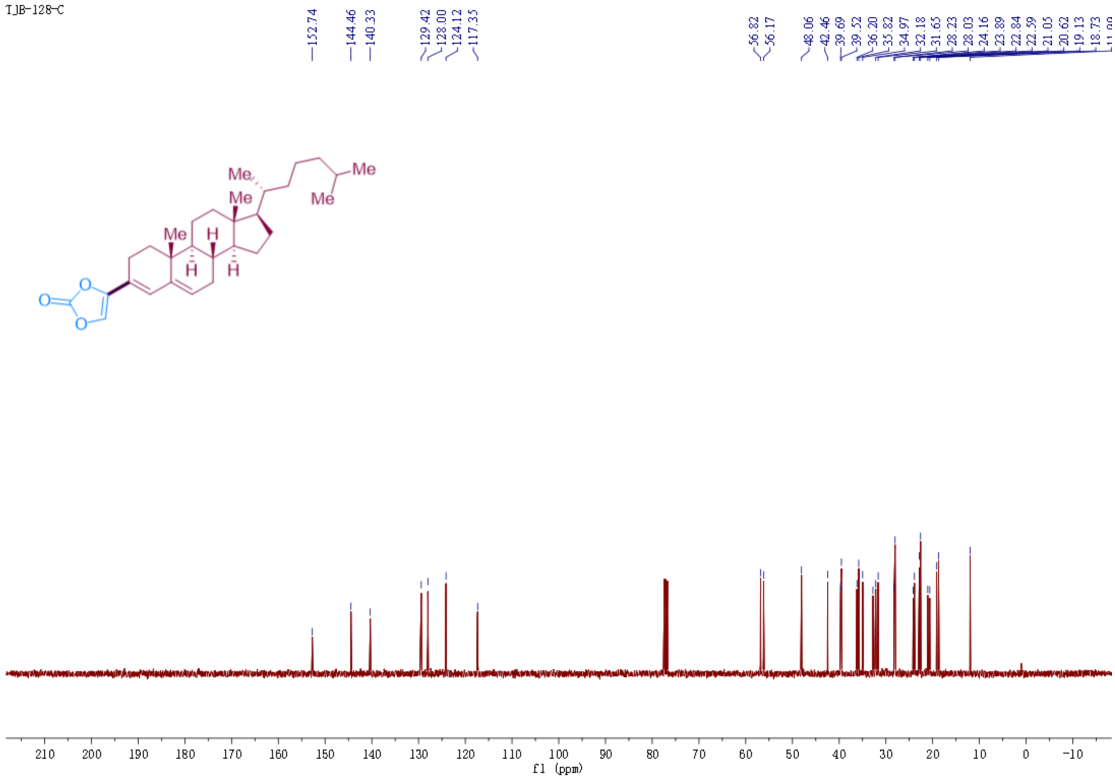
^{13}C NMR spectra of 3ab (101 MHz, $CDCl_3$)



^{1}H NMR spectra of 3ac (400 MHz, $CDCl_3$)



^{13}C NMR spectra of 3ac (101 MHz, $CDCl_3$)



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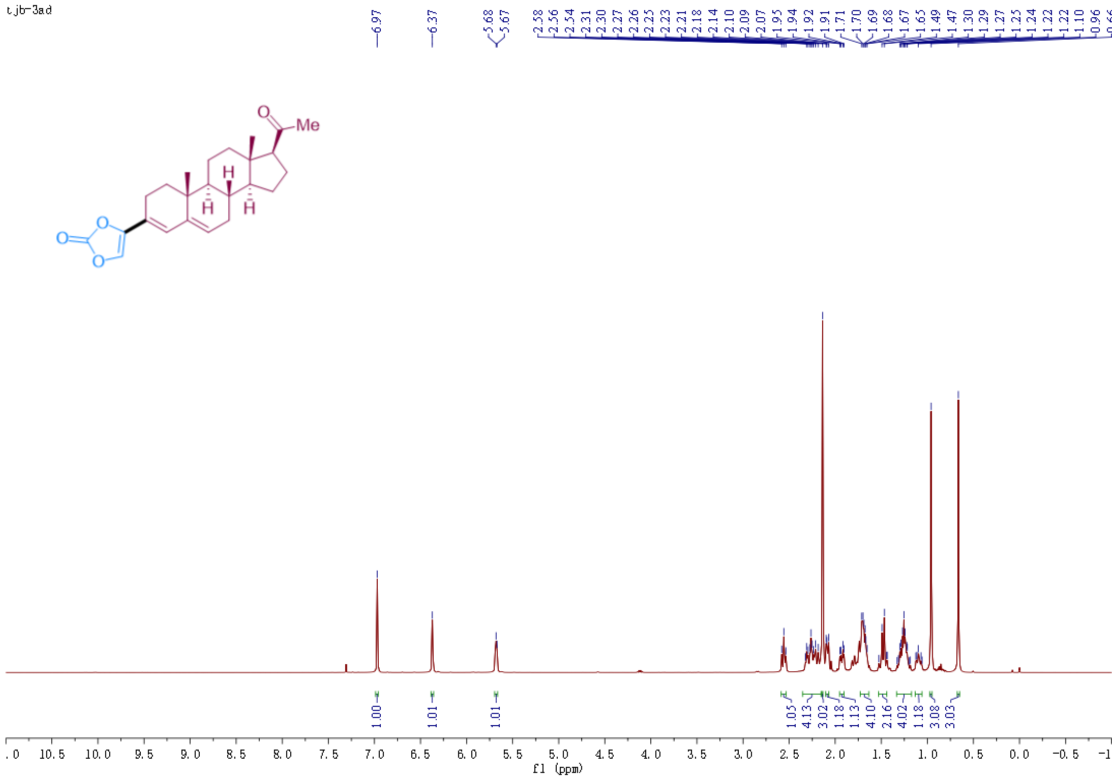
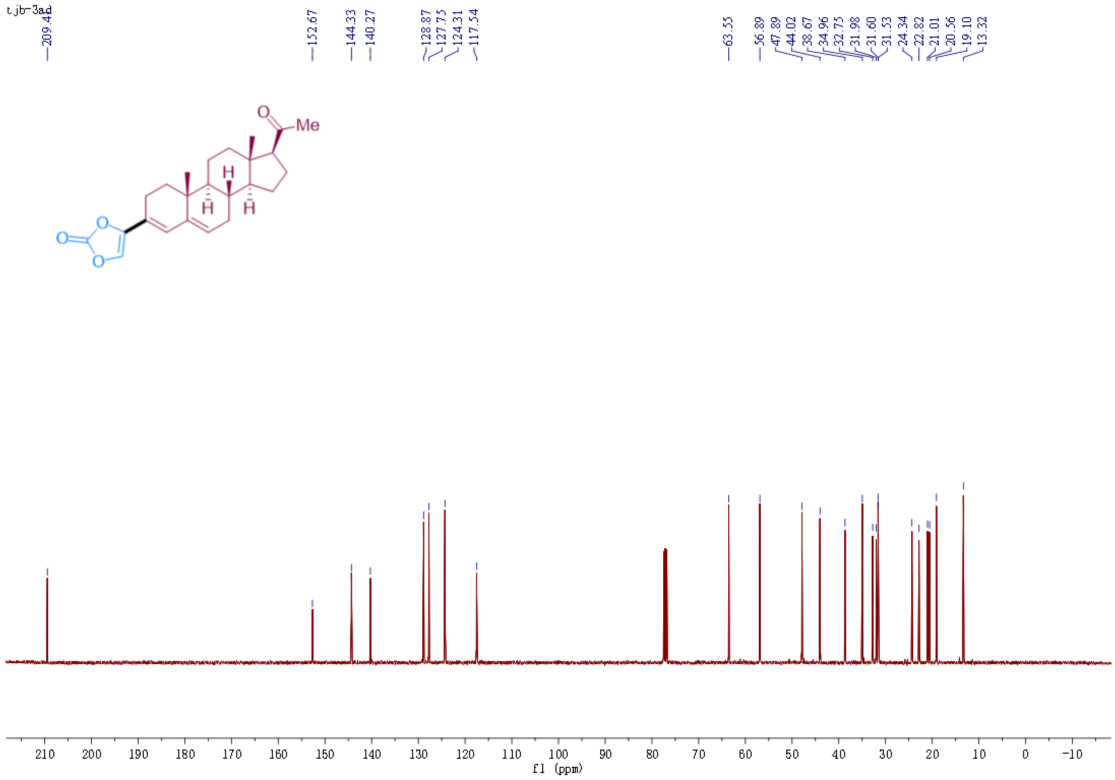
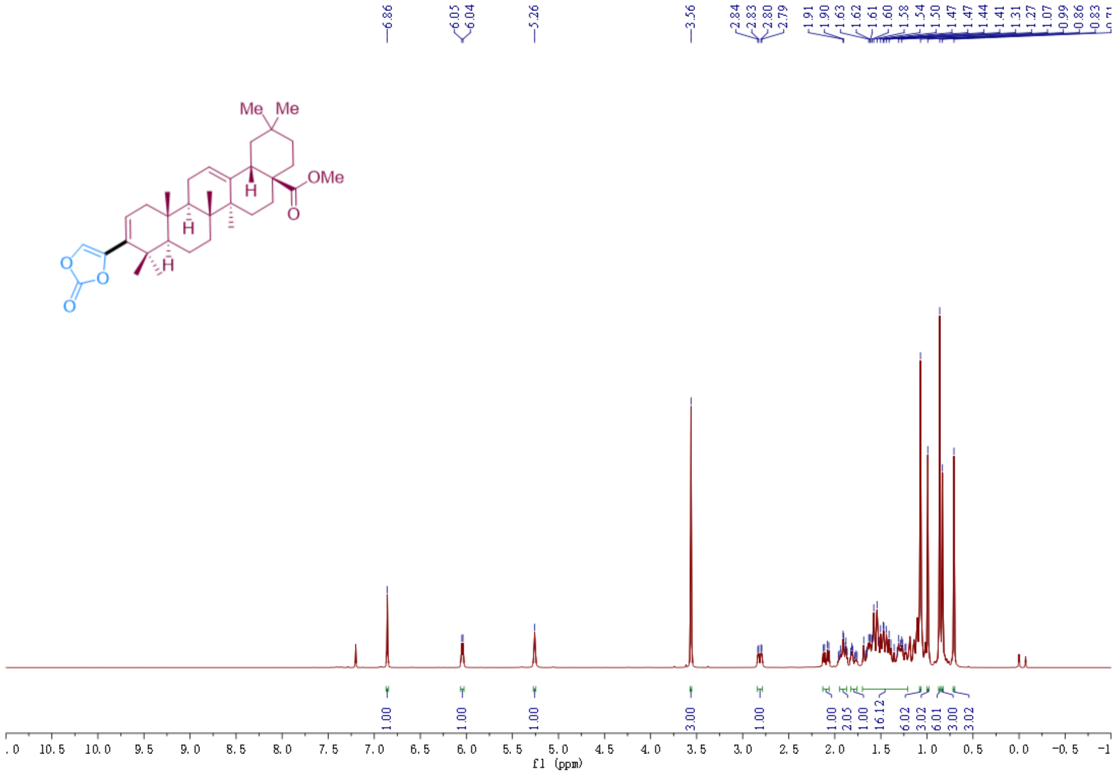


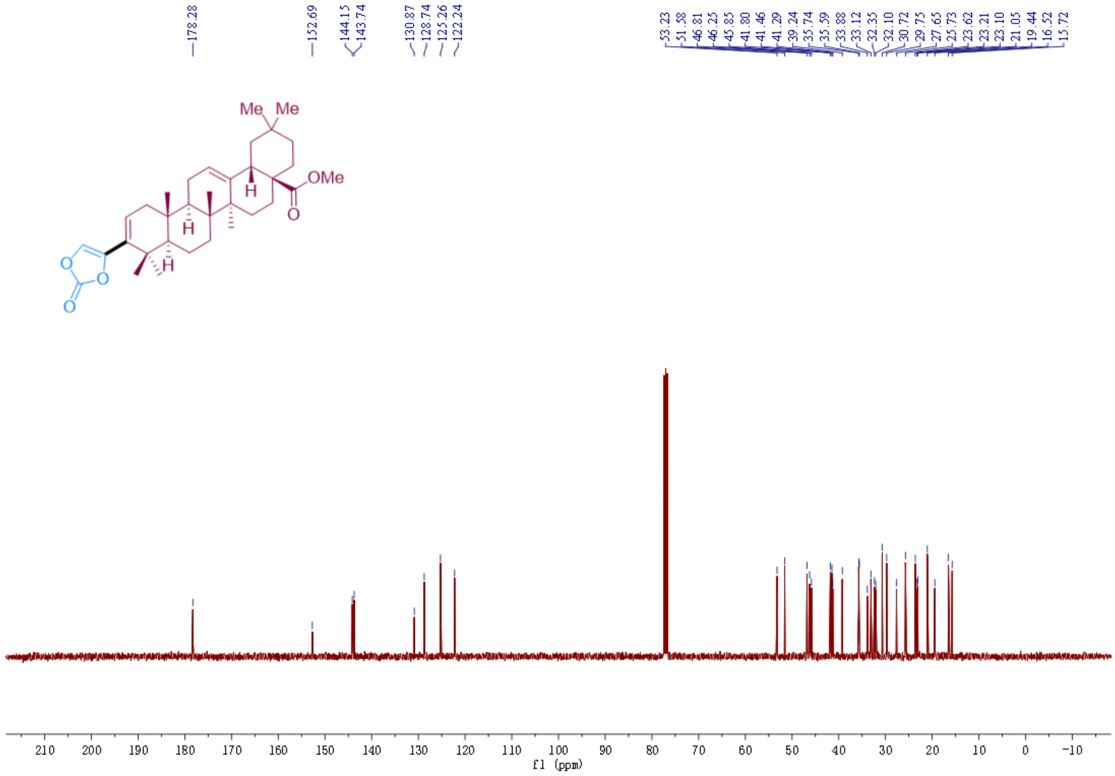
^{13}C NMR spectra of 3ad (101 MHz, CDCl$_3$)



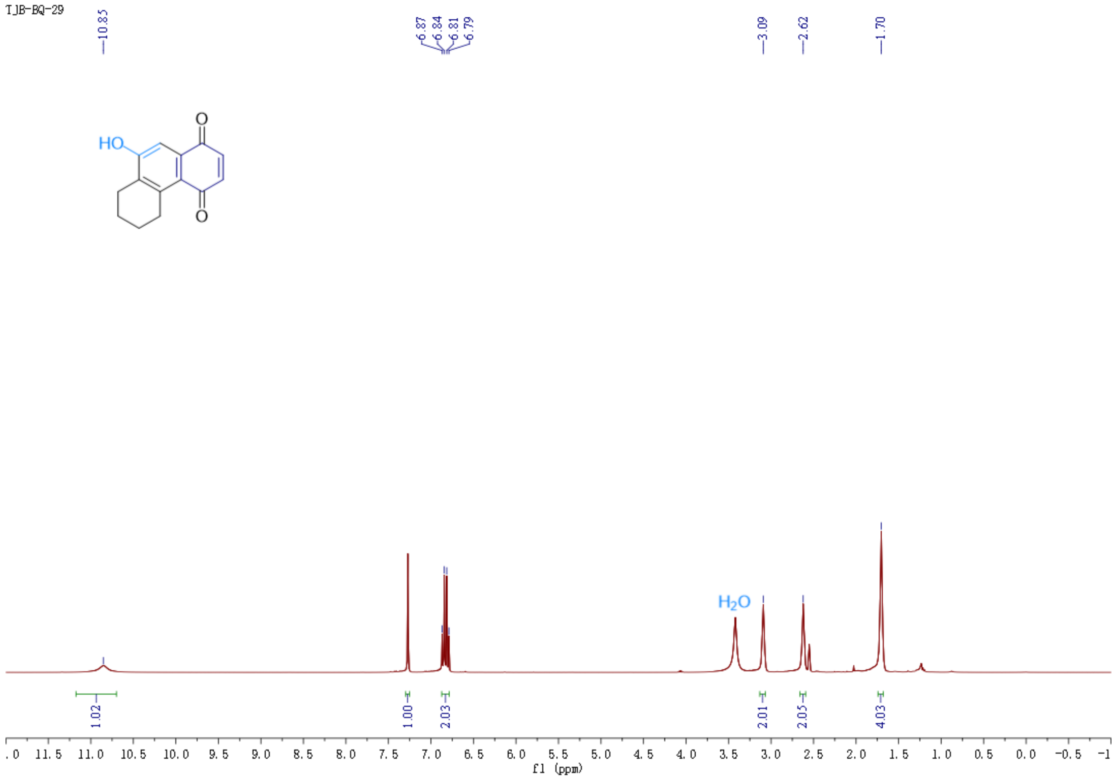
^{1}H NMR spectra of 3ae (400 MHz, CDCl$_3$)



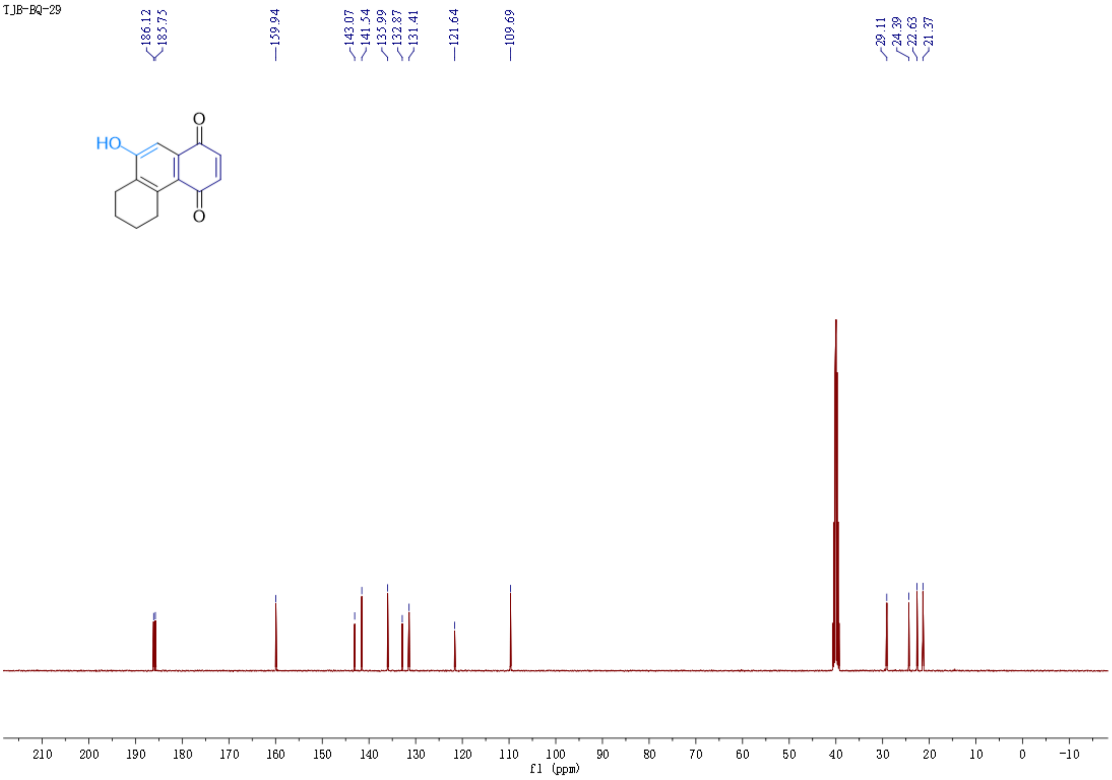
^{13}C NMR spectra of 3ae (101 MHz, $CDCl_3$)



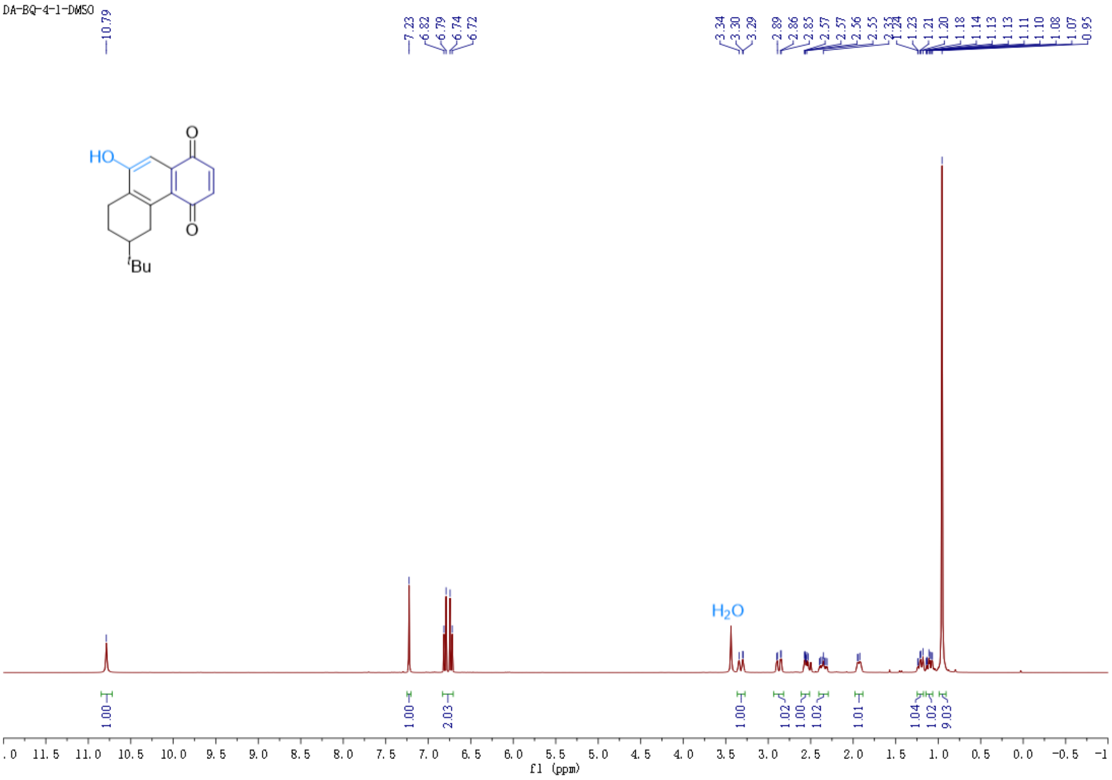
^{1}H NMR spectra of 5a (400 MHz, $(CD_3)_2SO$)



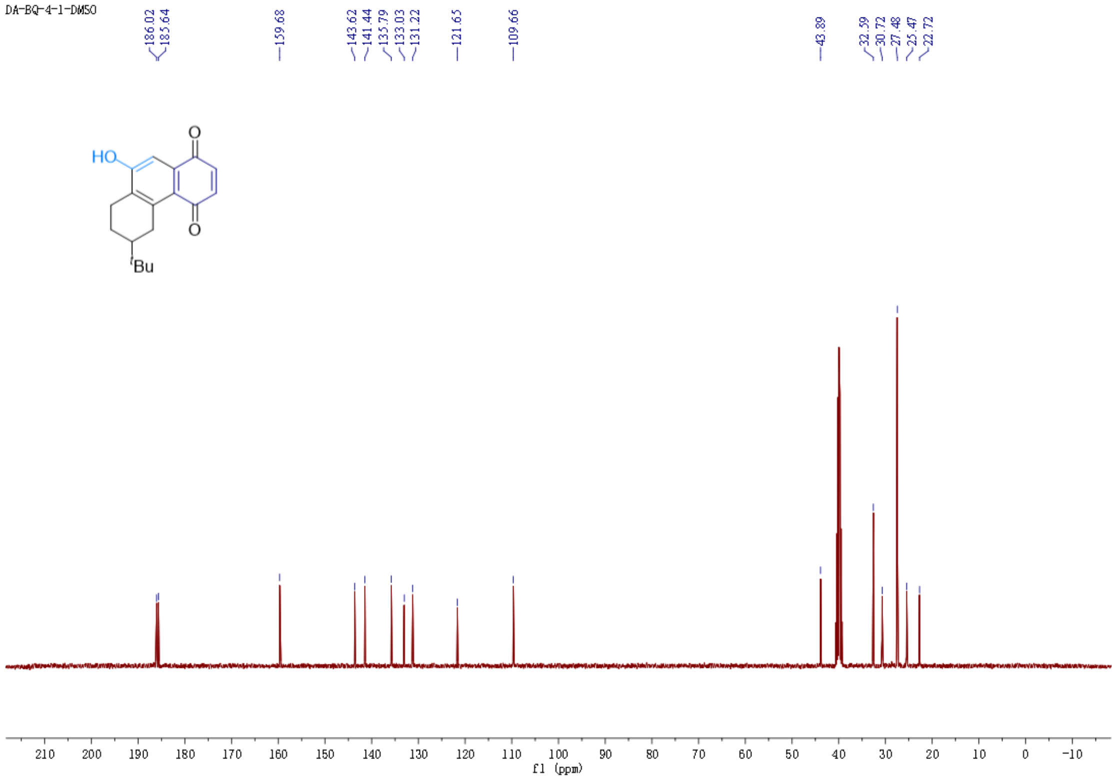
^{13}C NMR spectra of 5a (101 MHz, $(CD_3)_2SO$)



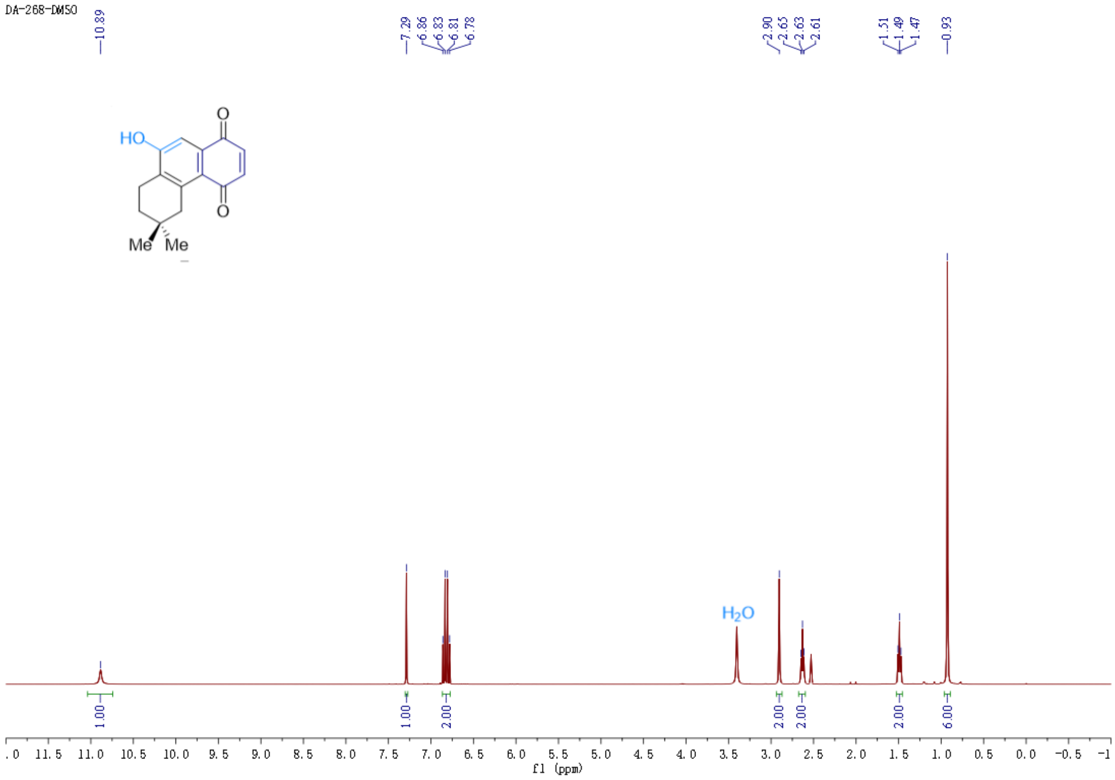
^{1}H NMR spectra of 5b (400 MHz, $(CD_3)_2SO$)



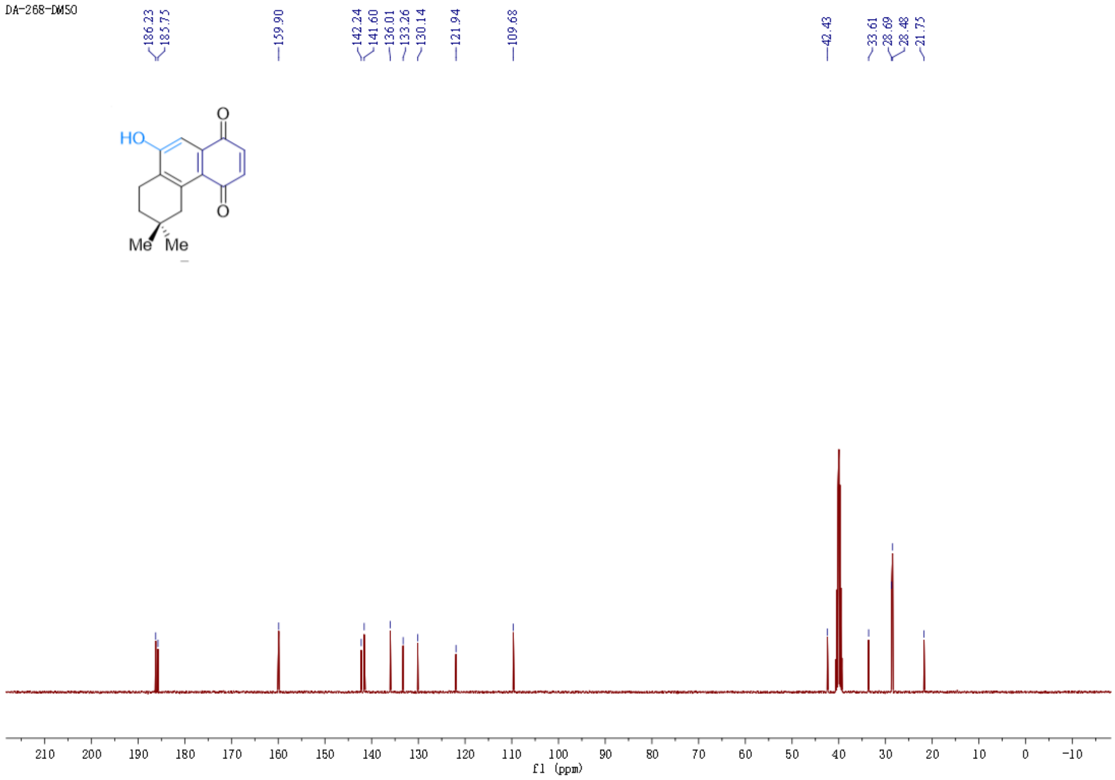
^{13}C NMR spectra of 5b (101 MHz, $(CD_3)_2SO$)



^{1}H NMR spectra of 5c (400 MHz, $(CD_3)_2SO$)



^{13}C NMR spectra of 5c (101 MHz, $(CD_3)_2SO$)



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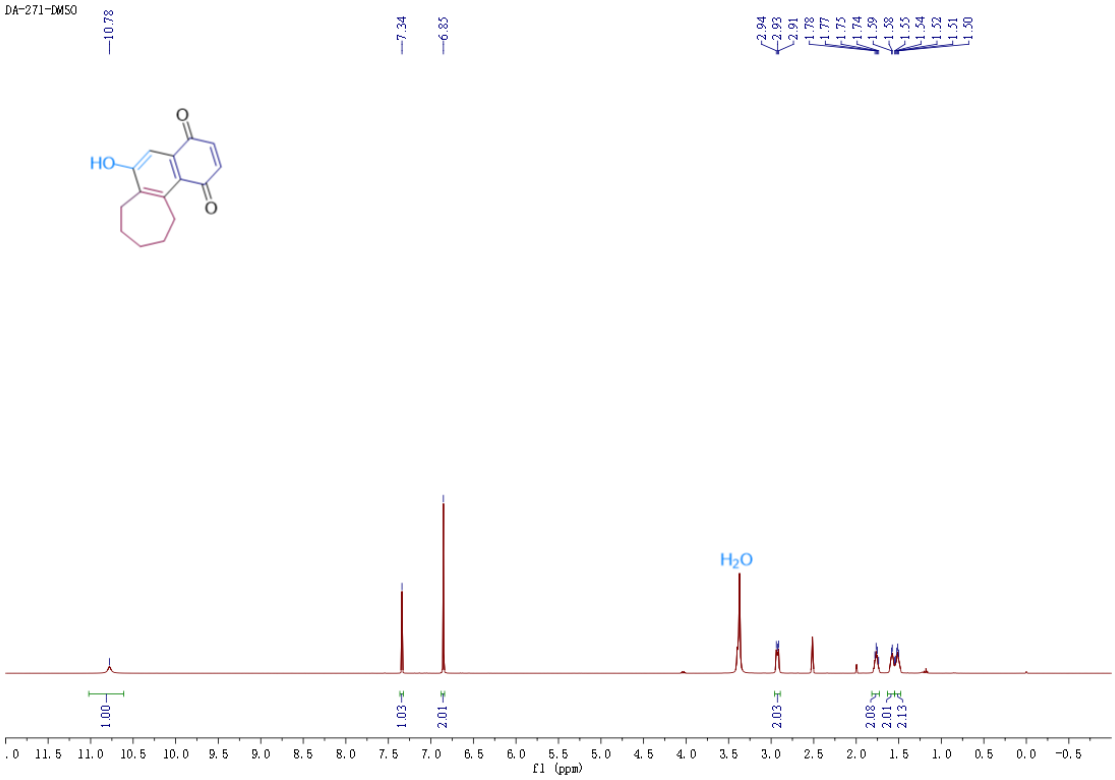

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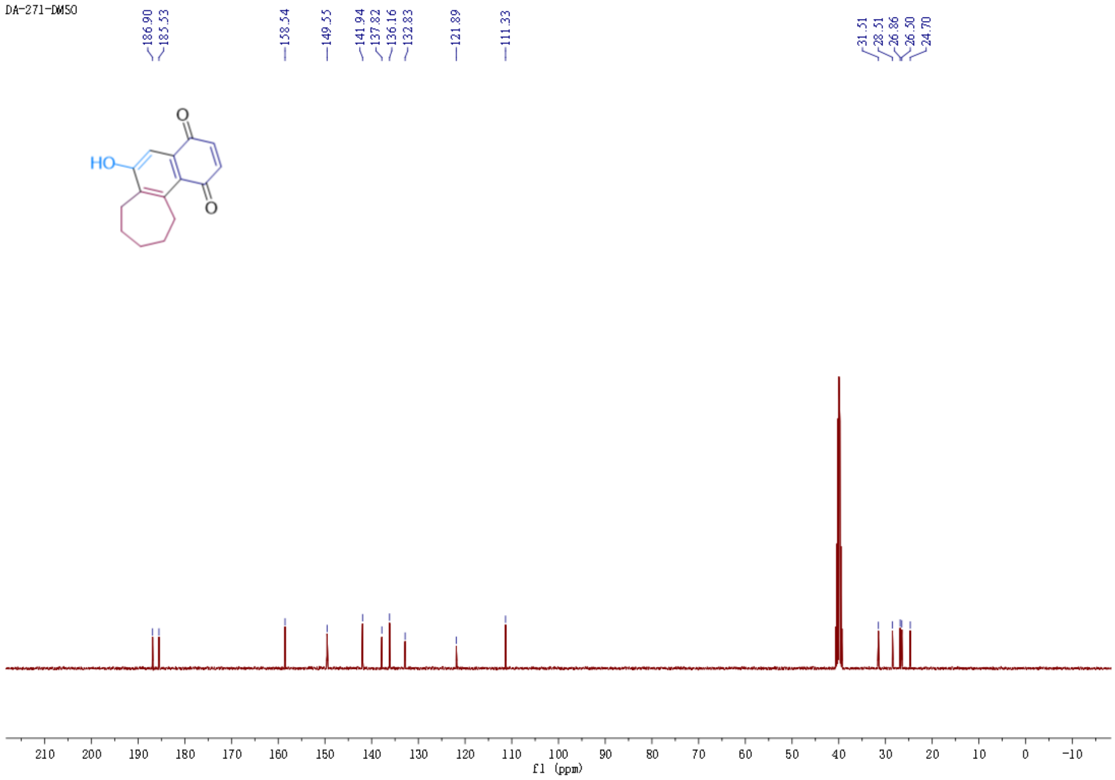
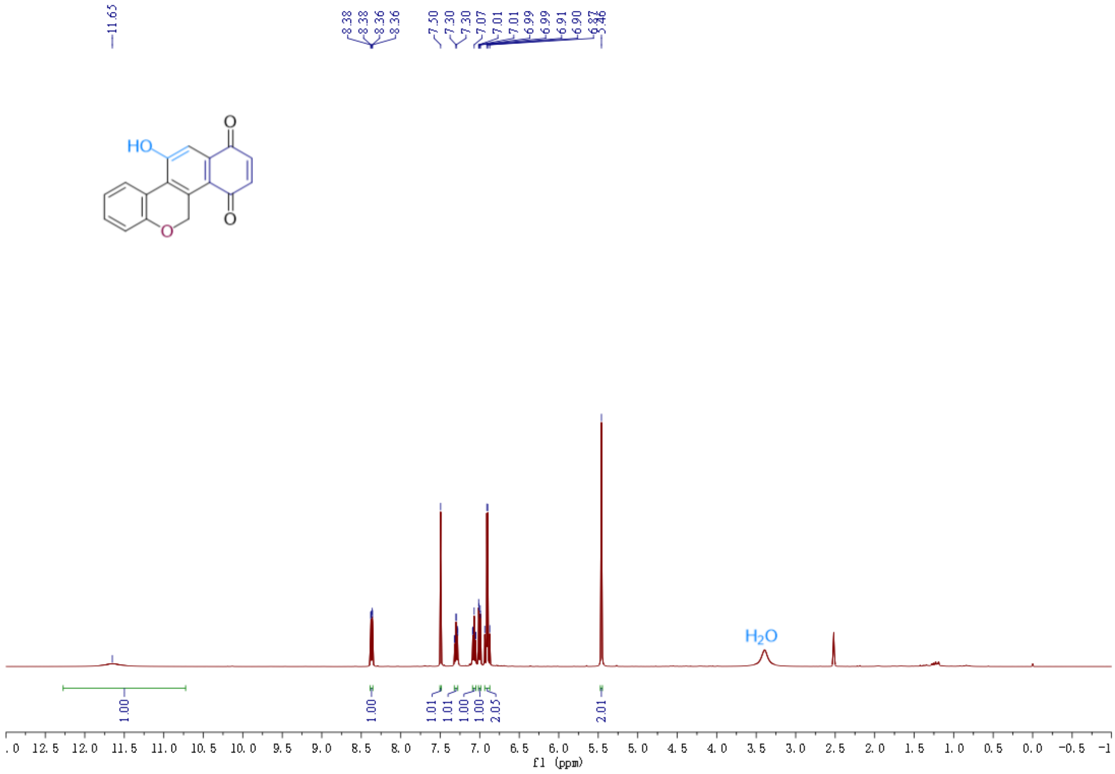
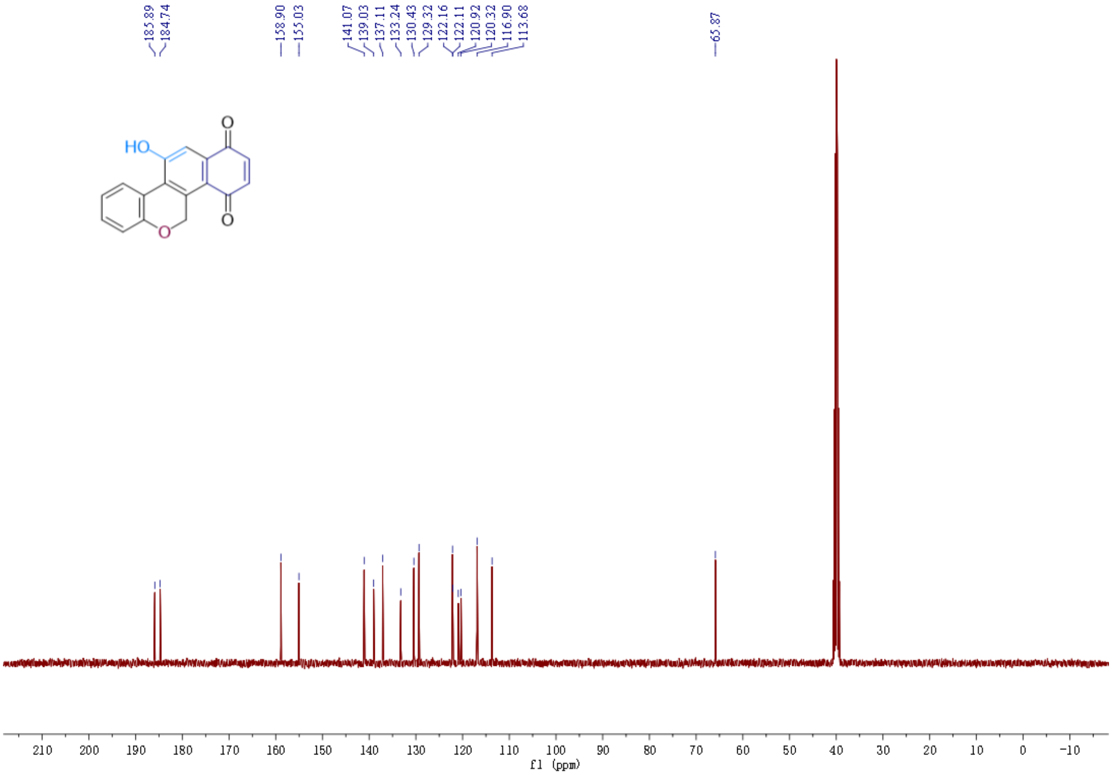


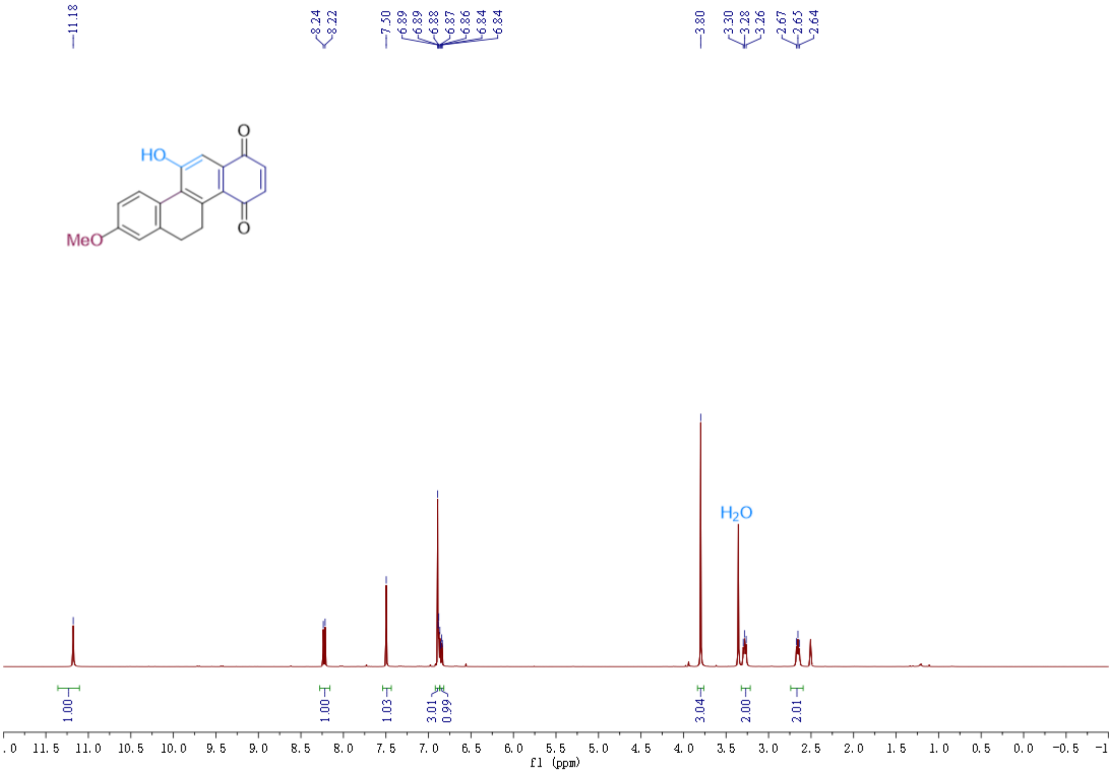
^1H NMR spectra of 5e (400 MHz, $(CD_3)_2SO$)



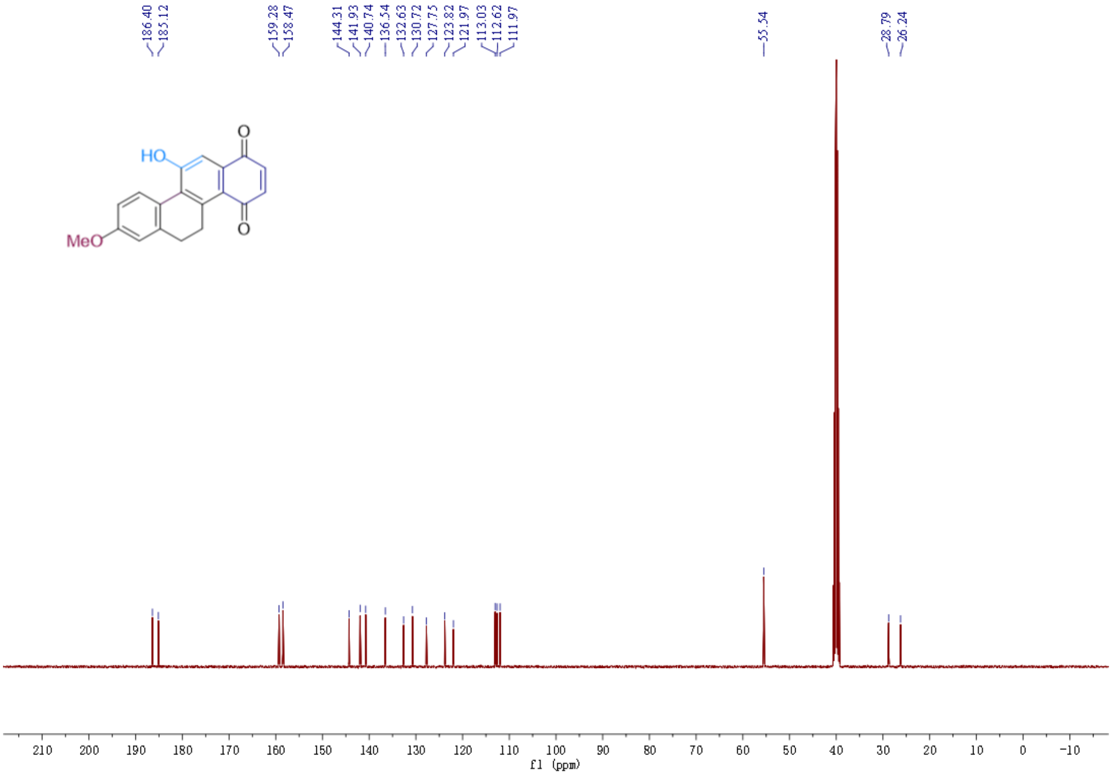
^{13}C NMR spectra of 5e (101 MHz, $(CD_3)_2SO$)



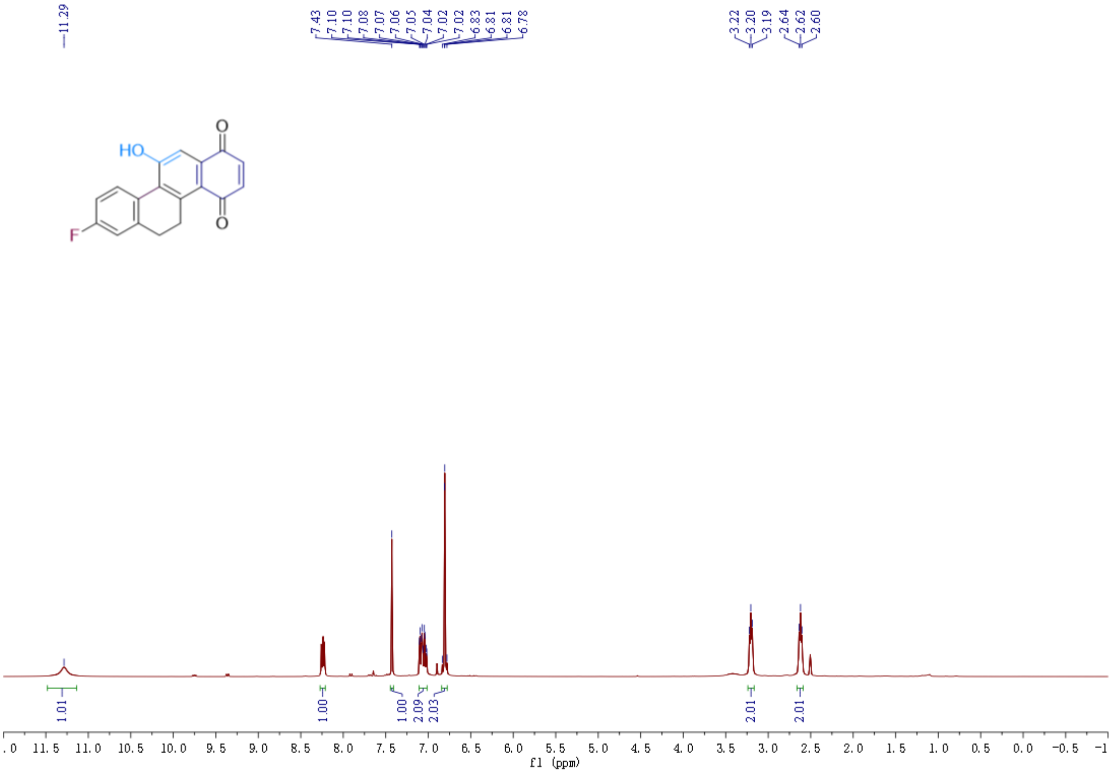
^{1}H NMR spectra of 5f (400 MHz, $(CD_3)_2SO$)



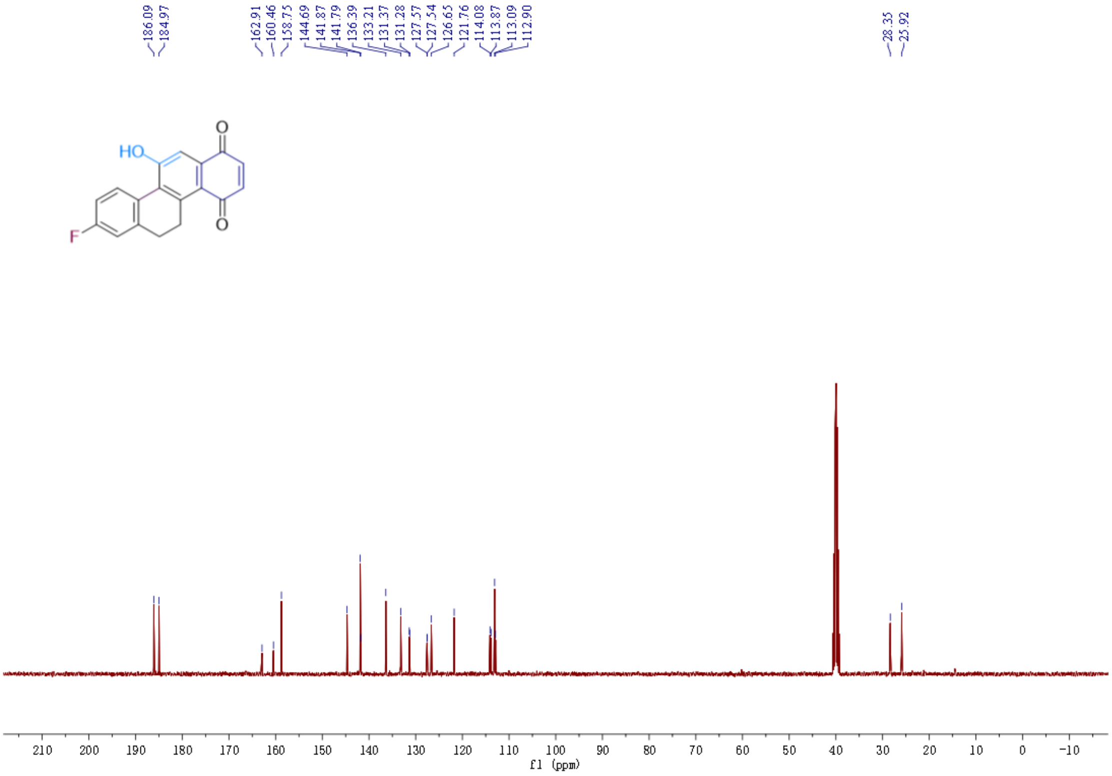
^{13}C NMR spectra of 5f (101 MHz, $(CD_3)_2SO$)



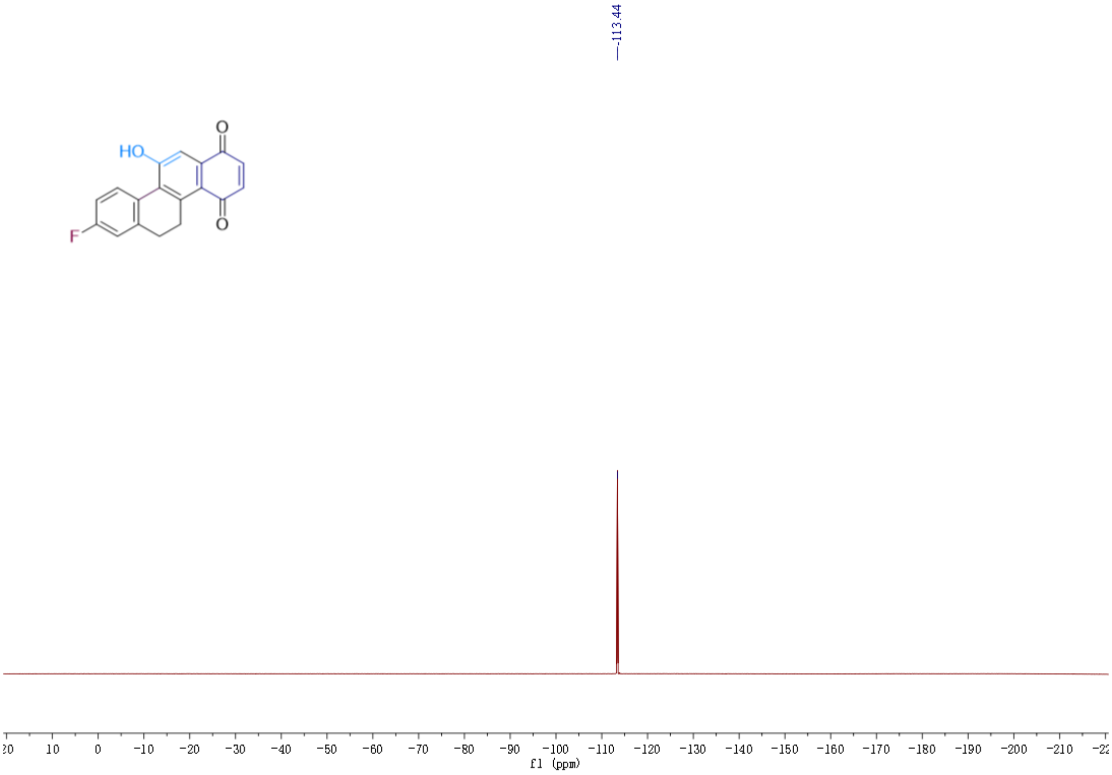
^{1}H NMR spectra of 5g (400 MHz, $(CD_3)_2SO$)



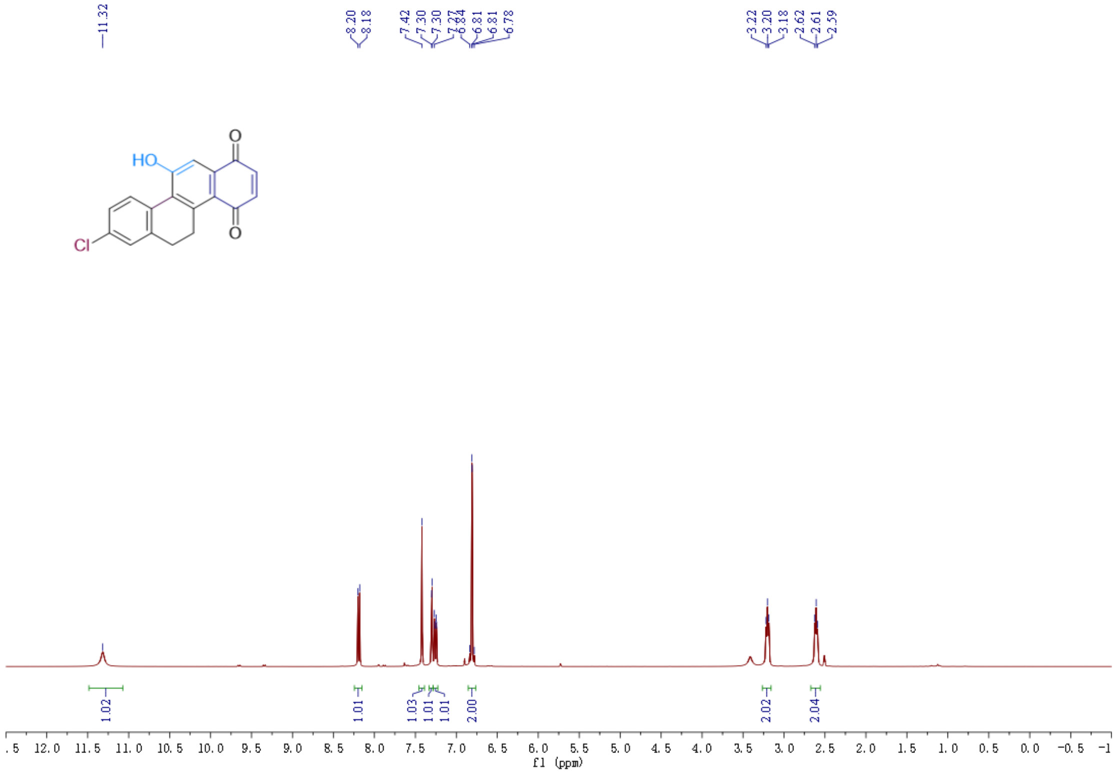
^{13}C NMR spectra of 5g (101 MHz, $(CD_3)_2SO$)



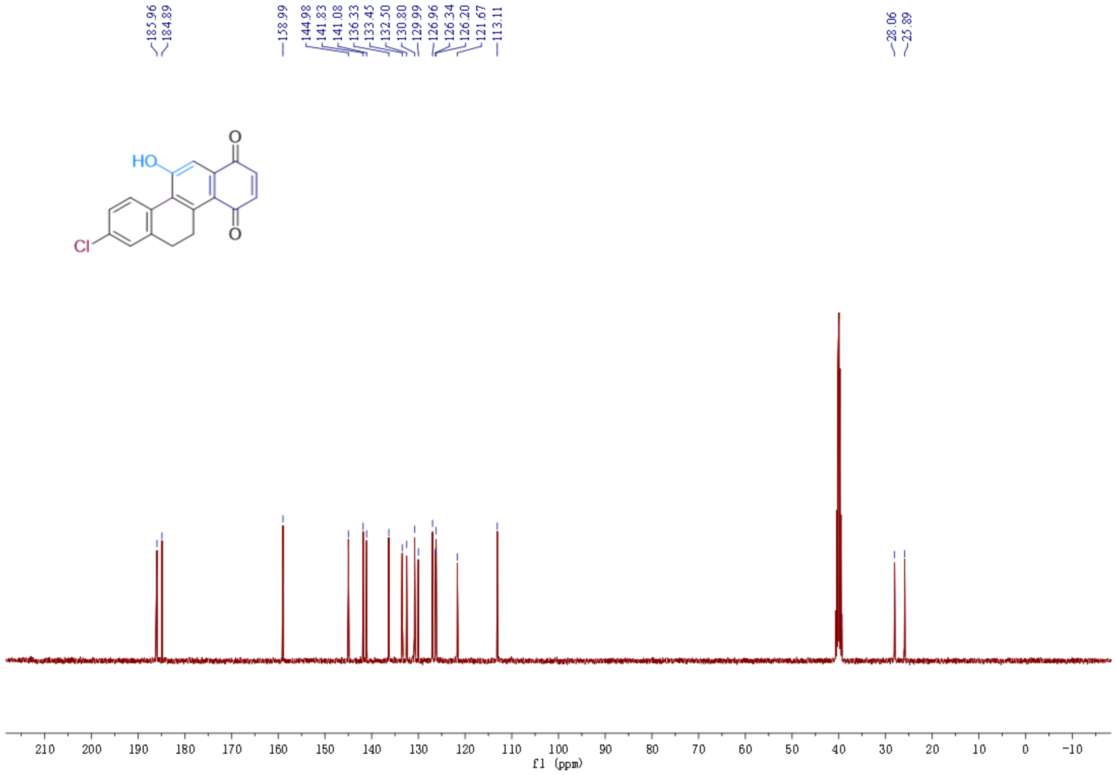
^{19}F NMR NMR spectra of 5g (377 MHz, $(CD_3)_2SO$)



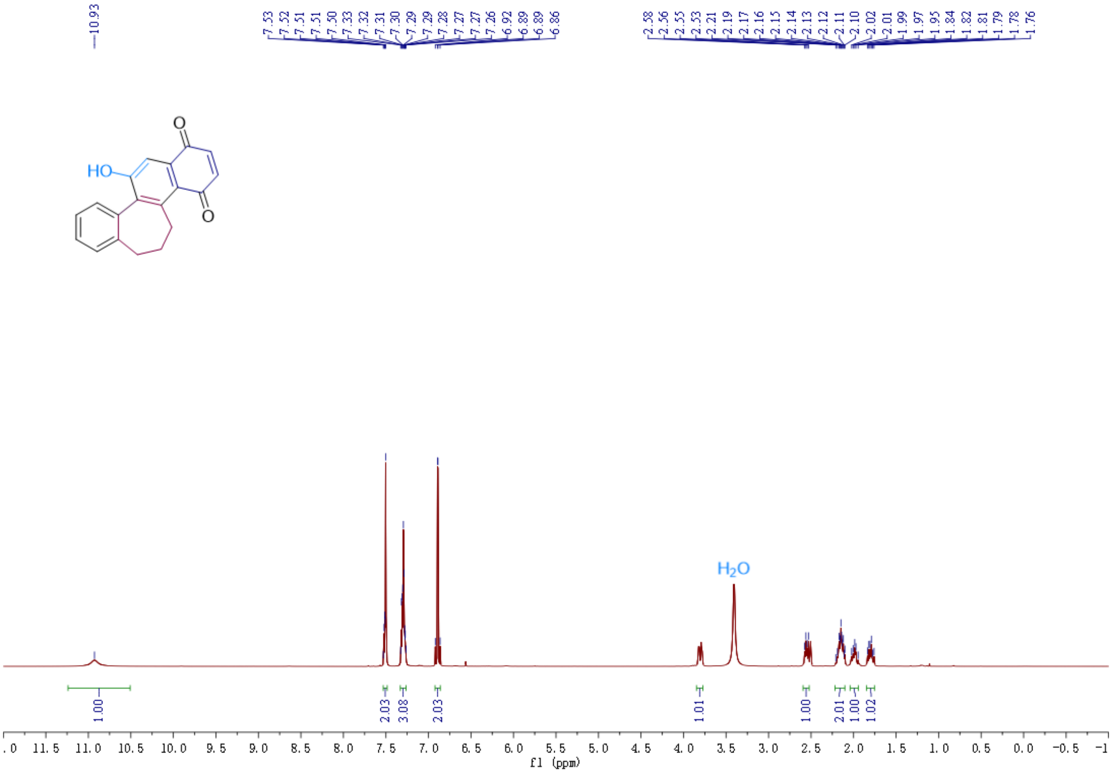
^{1}H NMR spectra of 5h (400 MHz, $(CD_3)_2SO$)



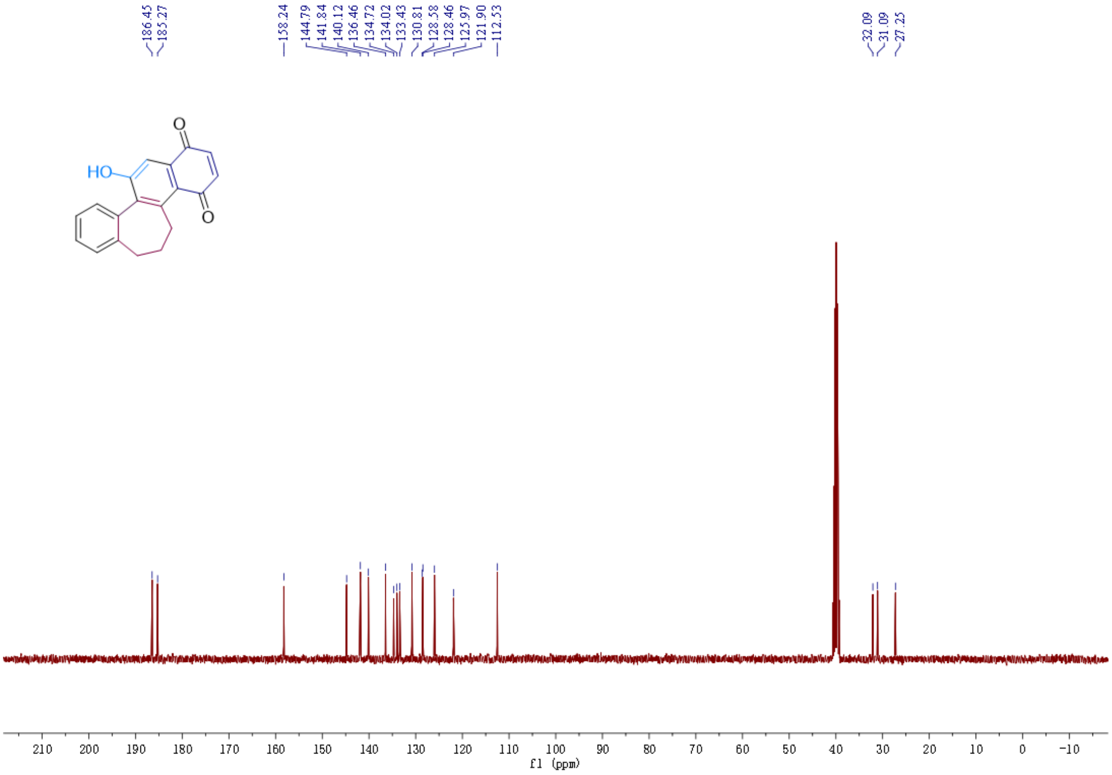
^{13}C NMR spectra of 5h (101 MHz, $(CD_3)_2SO$)



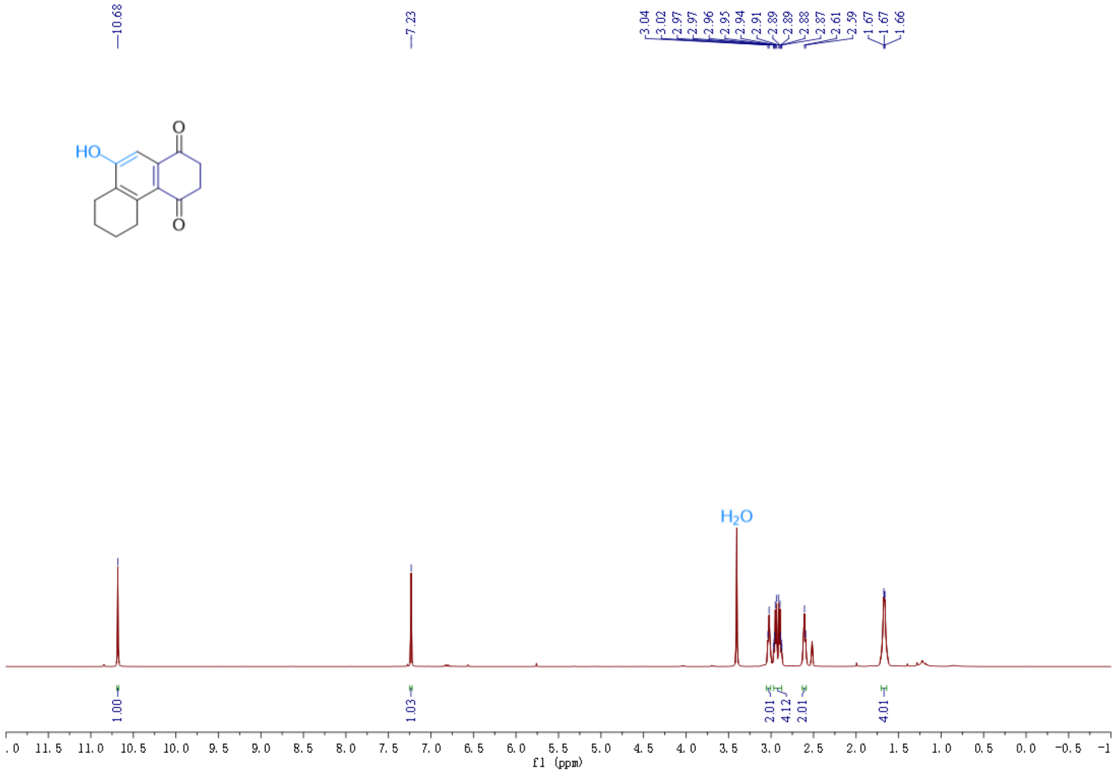
^{1}H NMR spectra of 5i (400 MHz, $(CD_3)_2SO$)



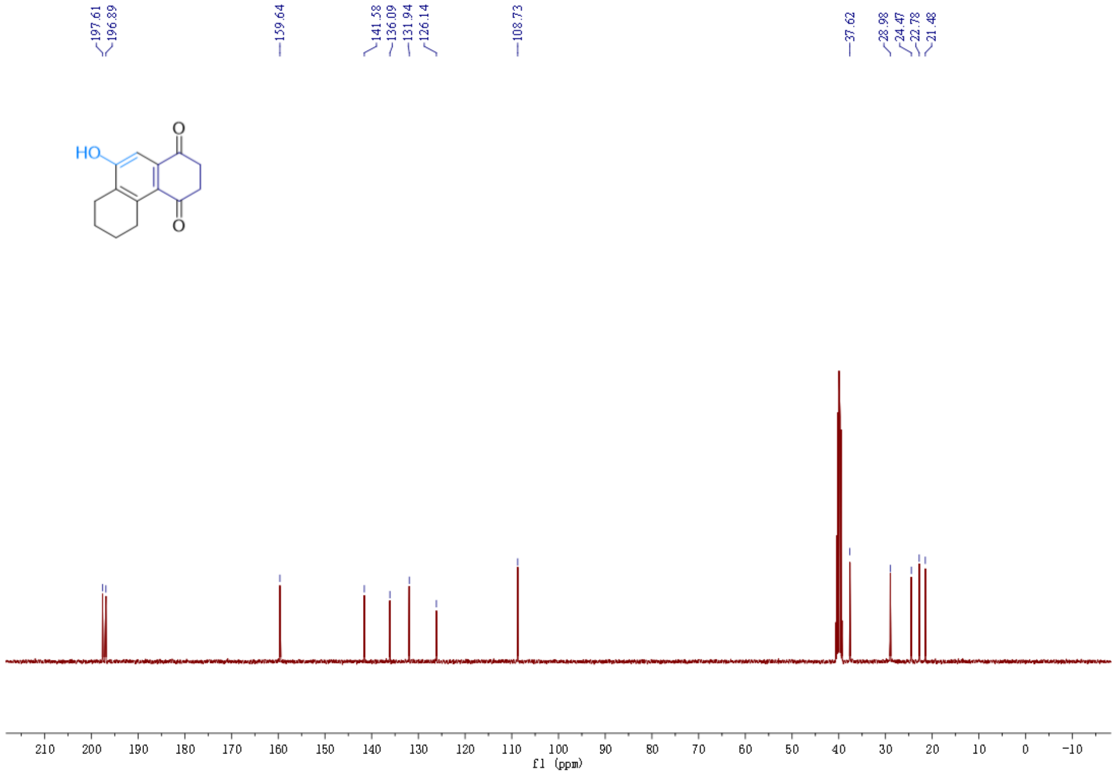
^{13}C NMR spectra of 5i (101 MHz, $(CD_3)_2SO$)



^{1}H NMR spectra of 6a (400 MHz, (CD$_3$)$_2$SO)



^{13}C NMR spectra of 6a (101 MHz, (CD$_3$)$_2$SO)



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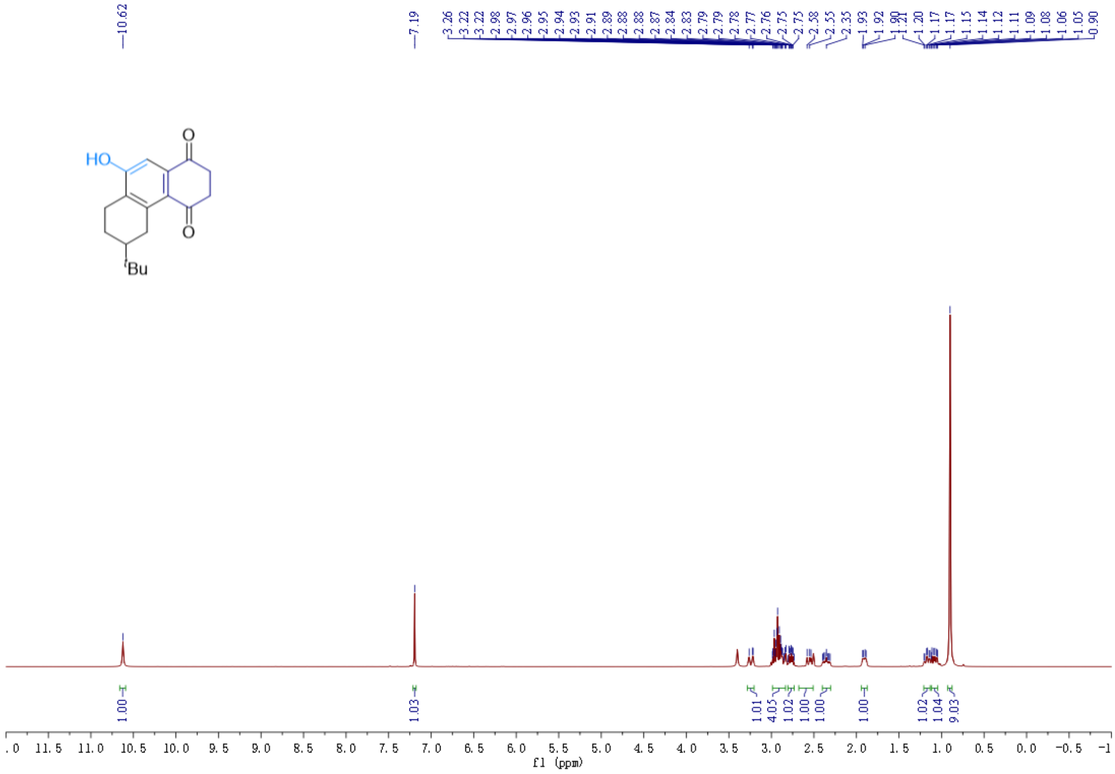

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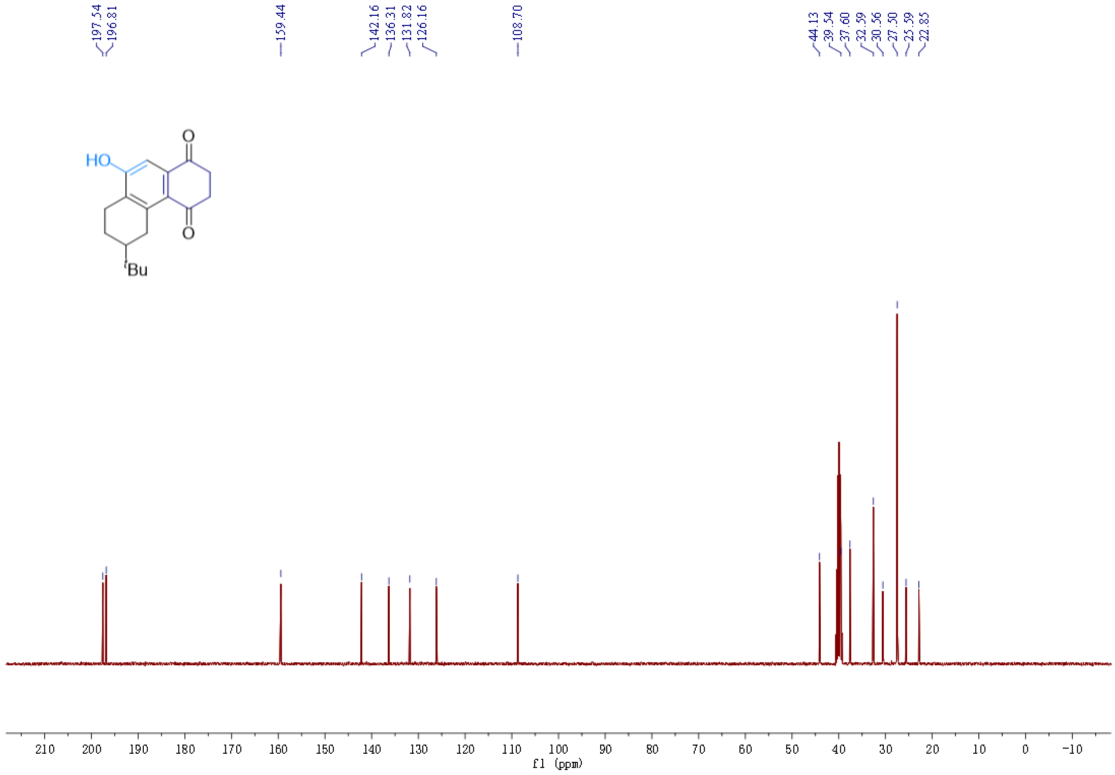

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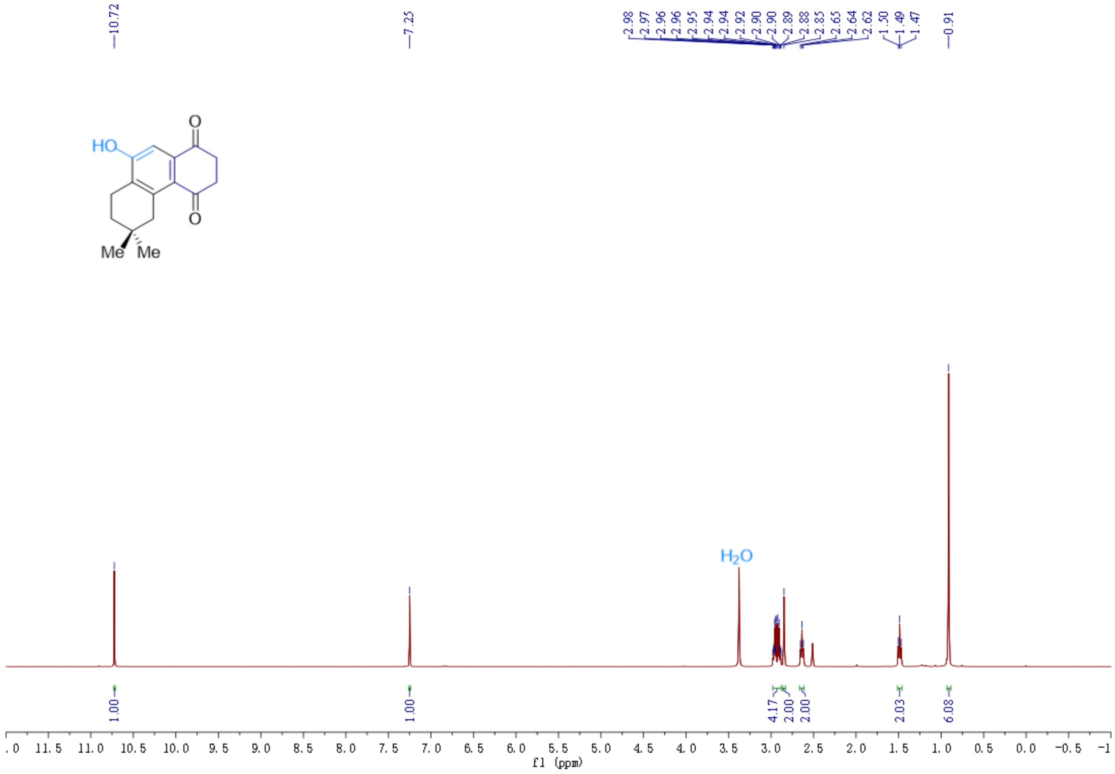

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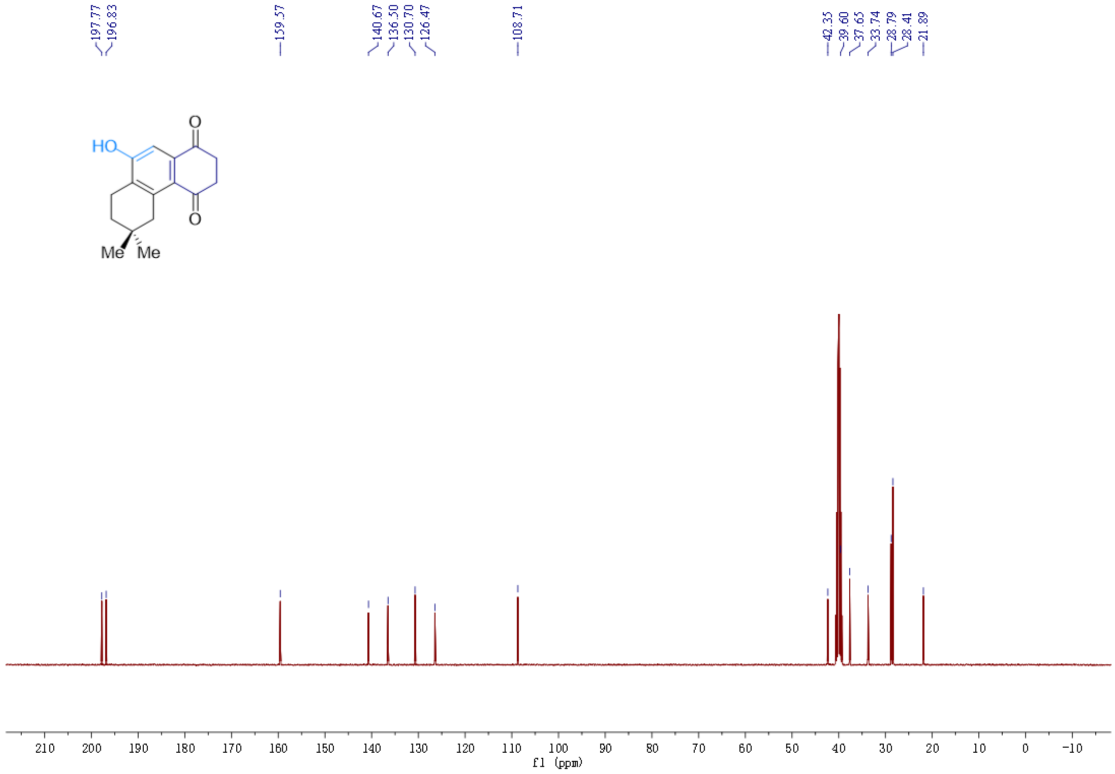

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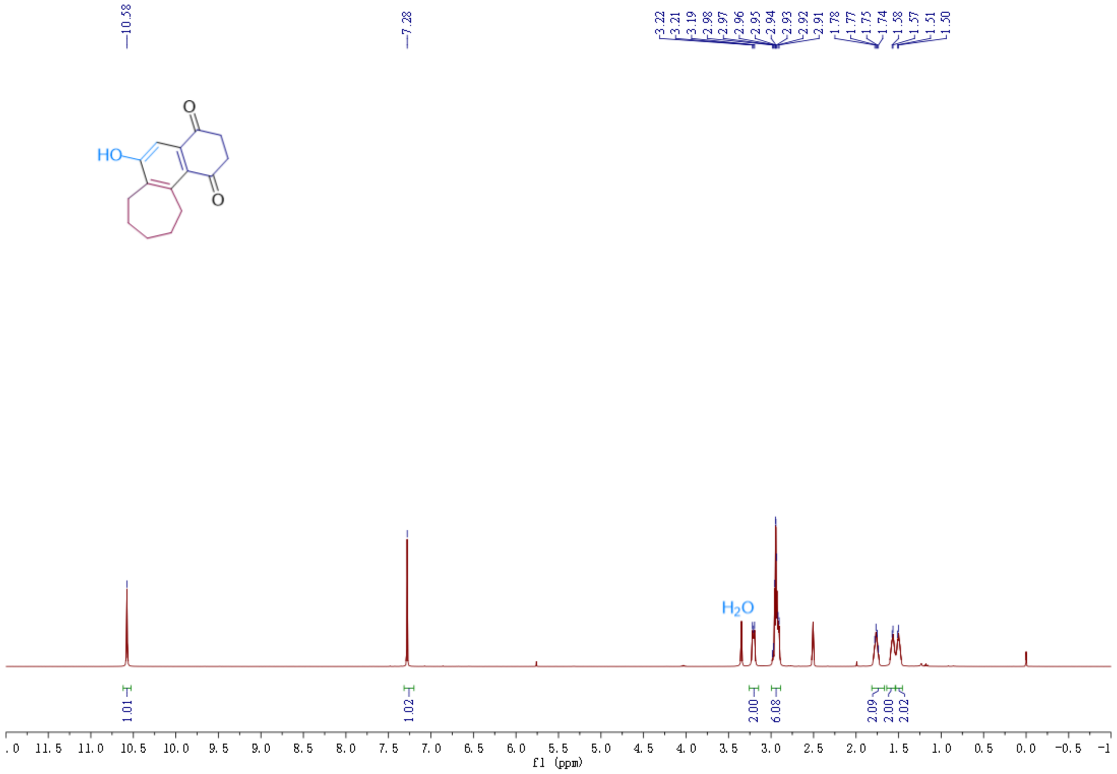

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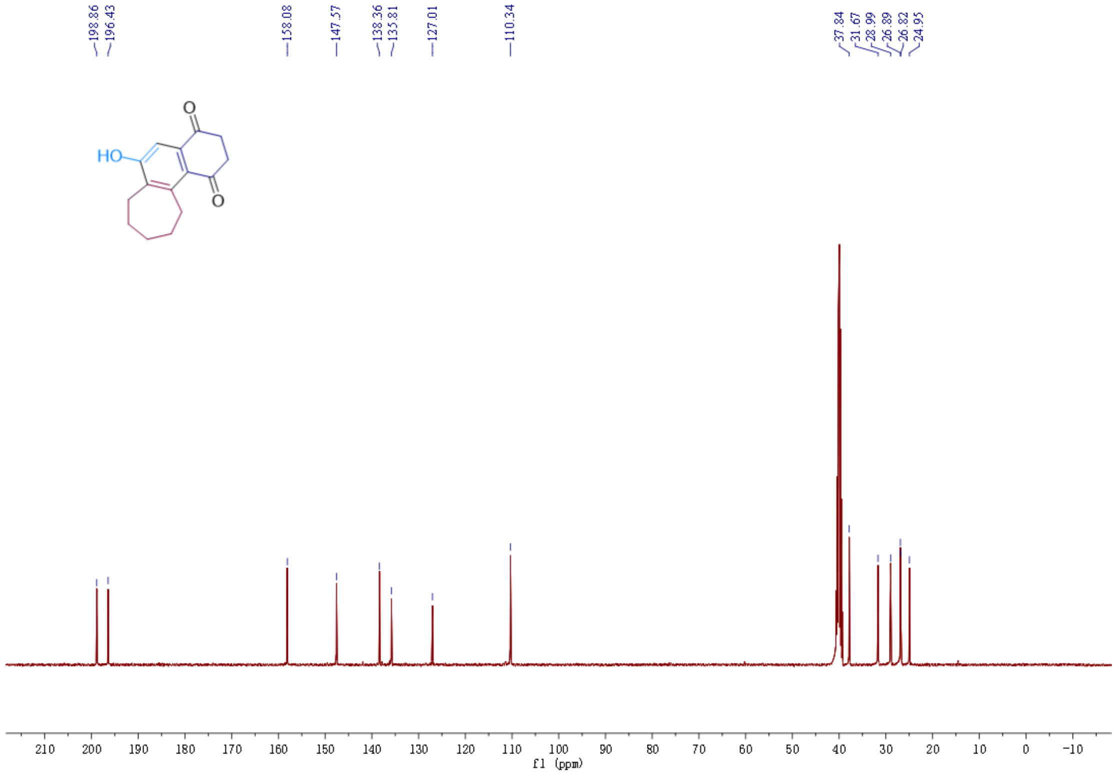

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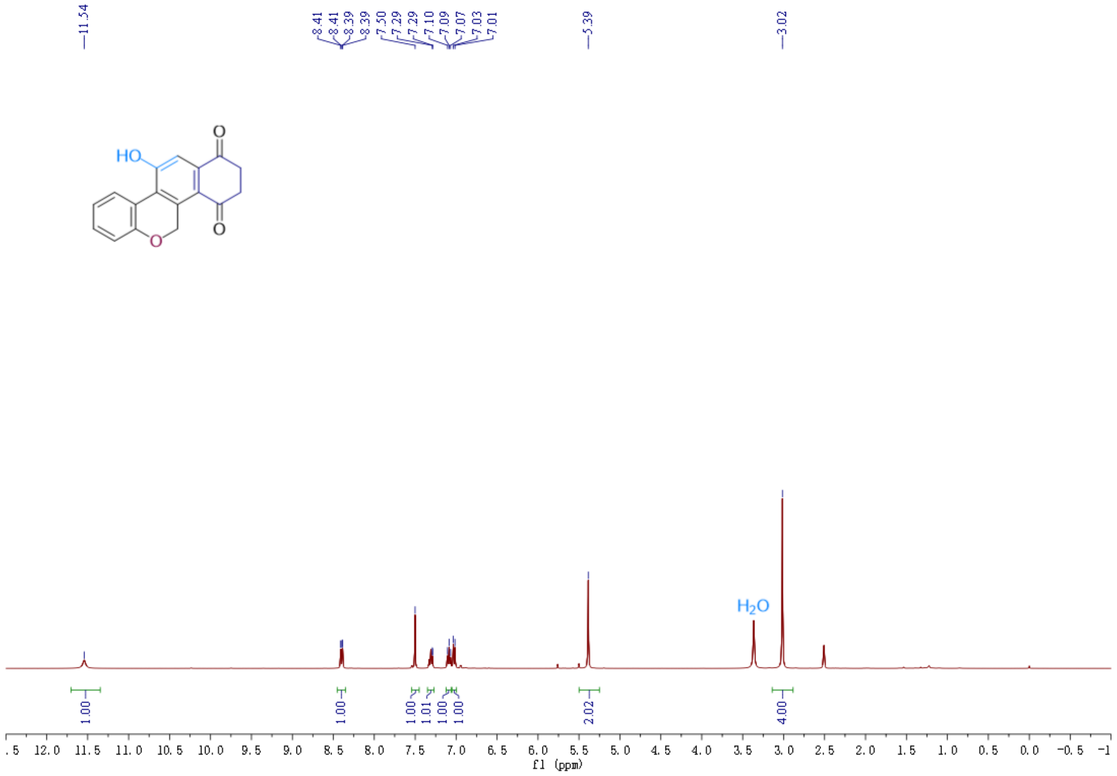

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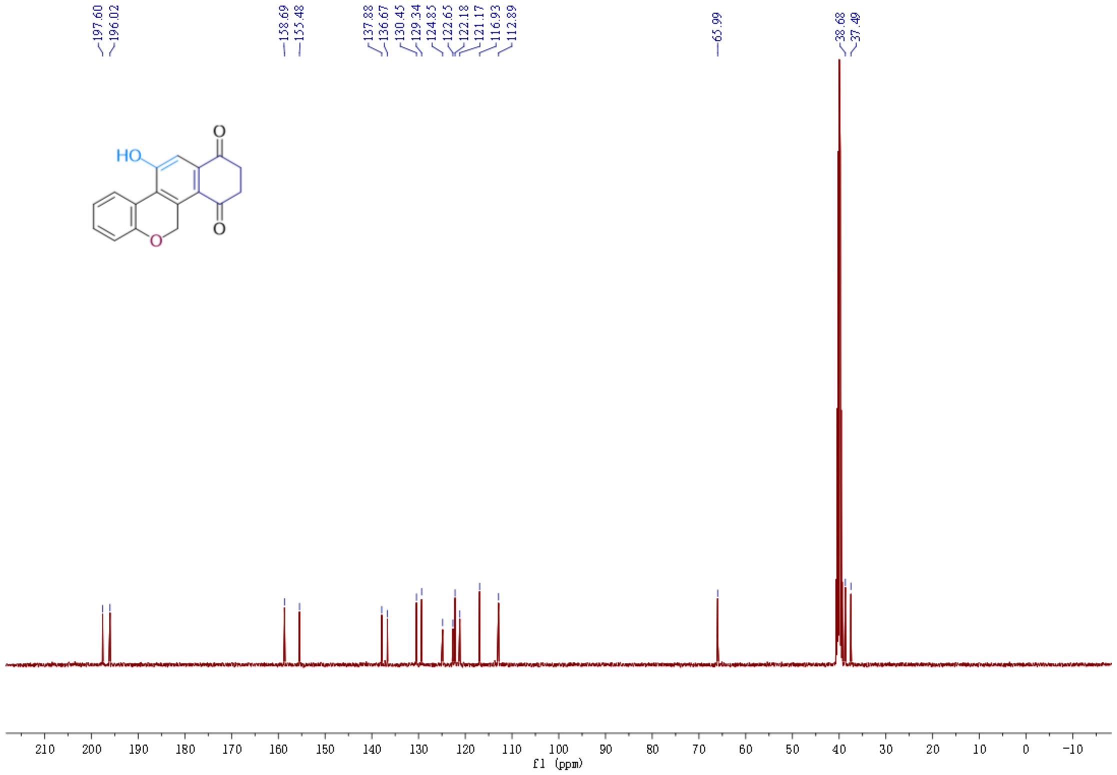

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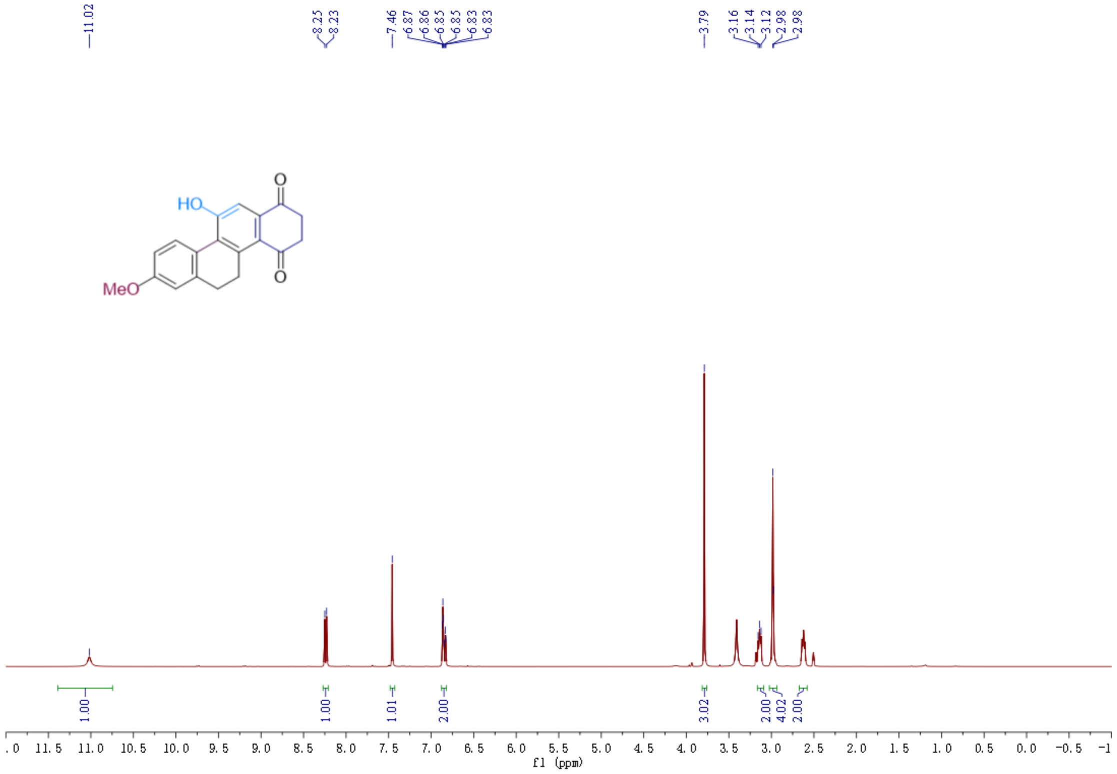

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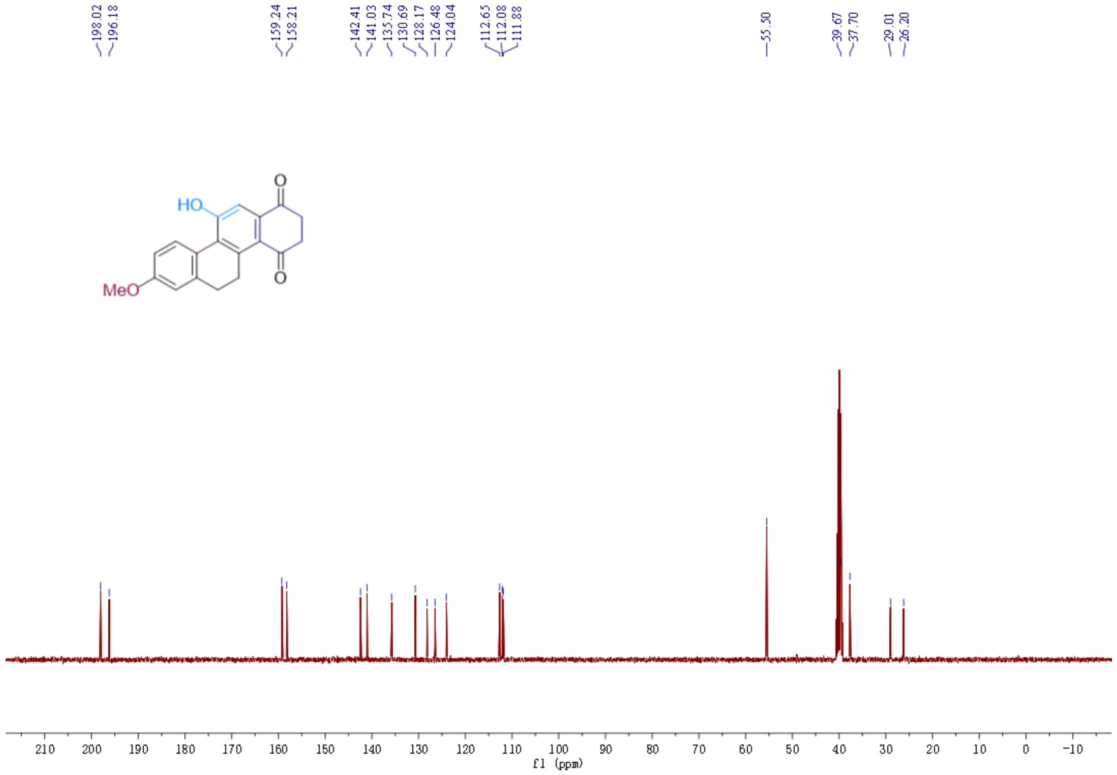

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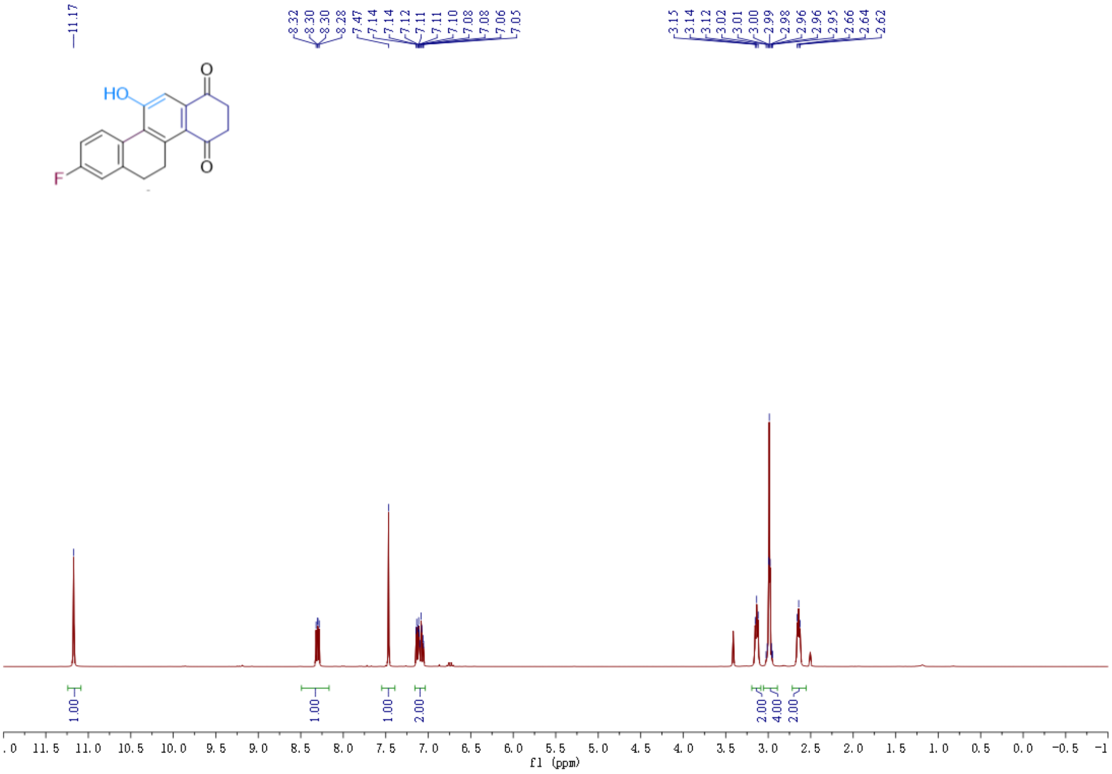

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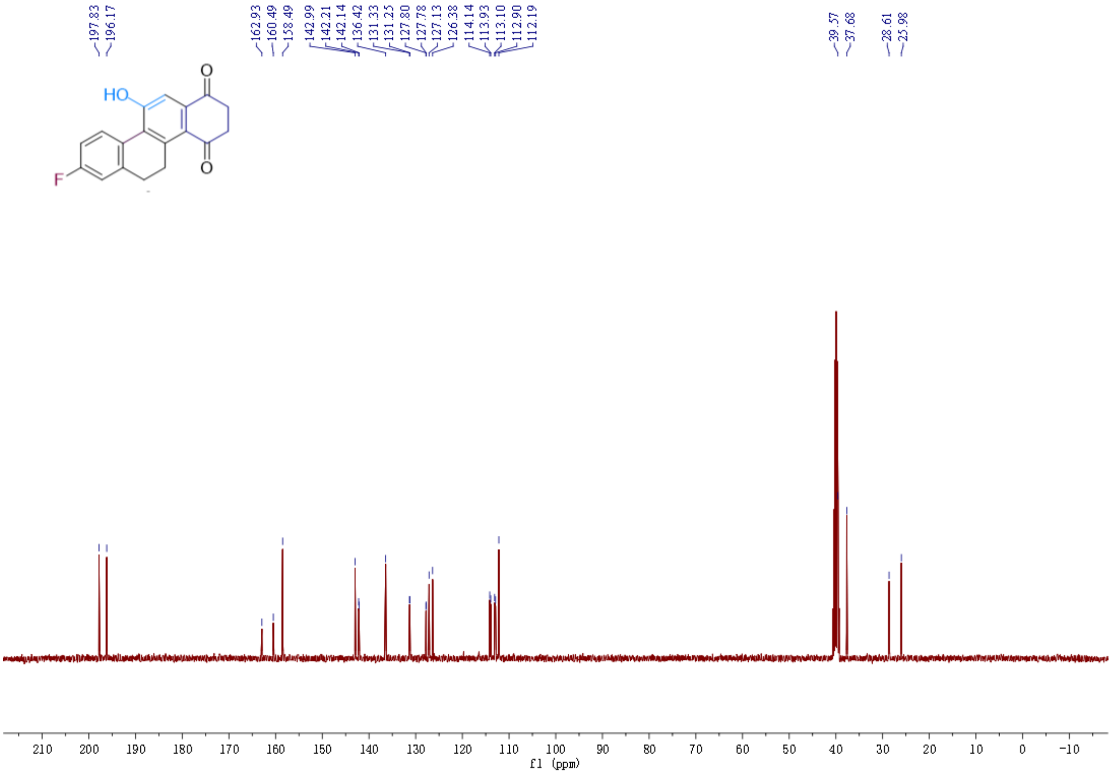
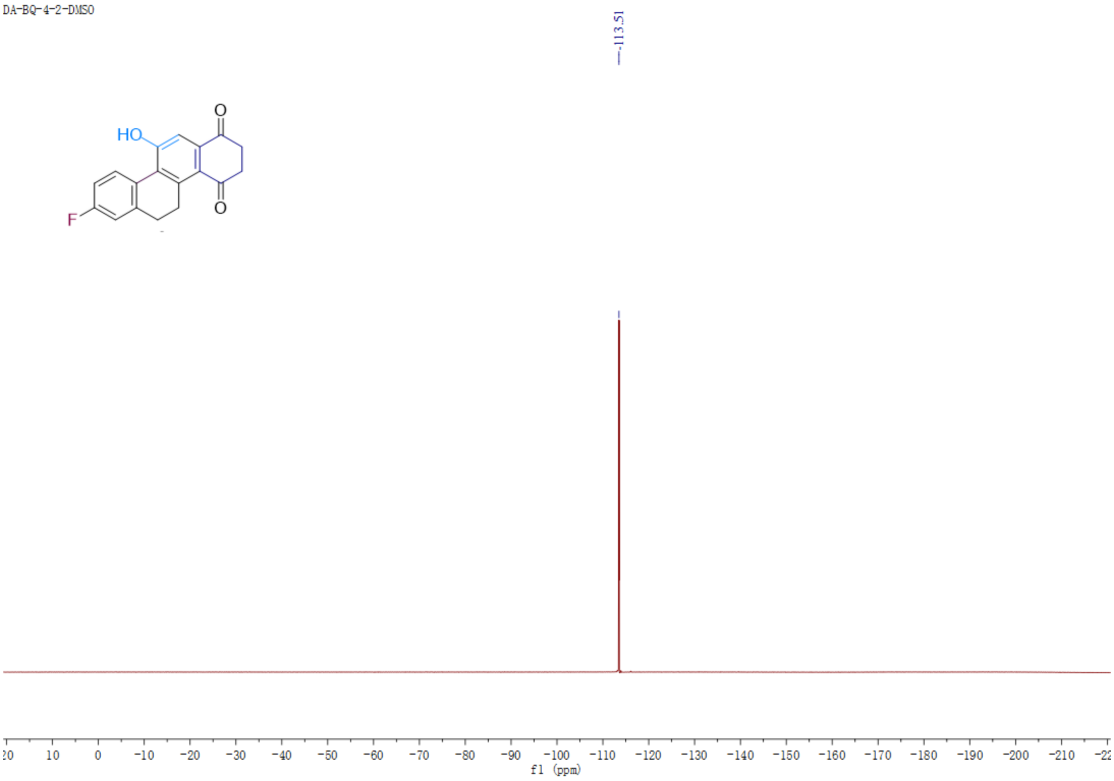


^{19}F NMR NMR spectra of 6g (377 MHz, $(CD_3)_2SO$)



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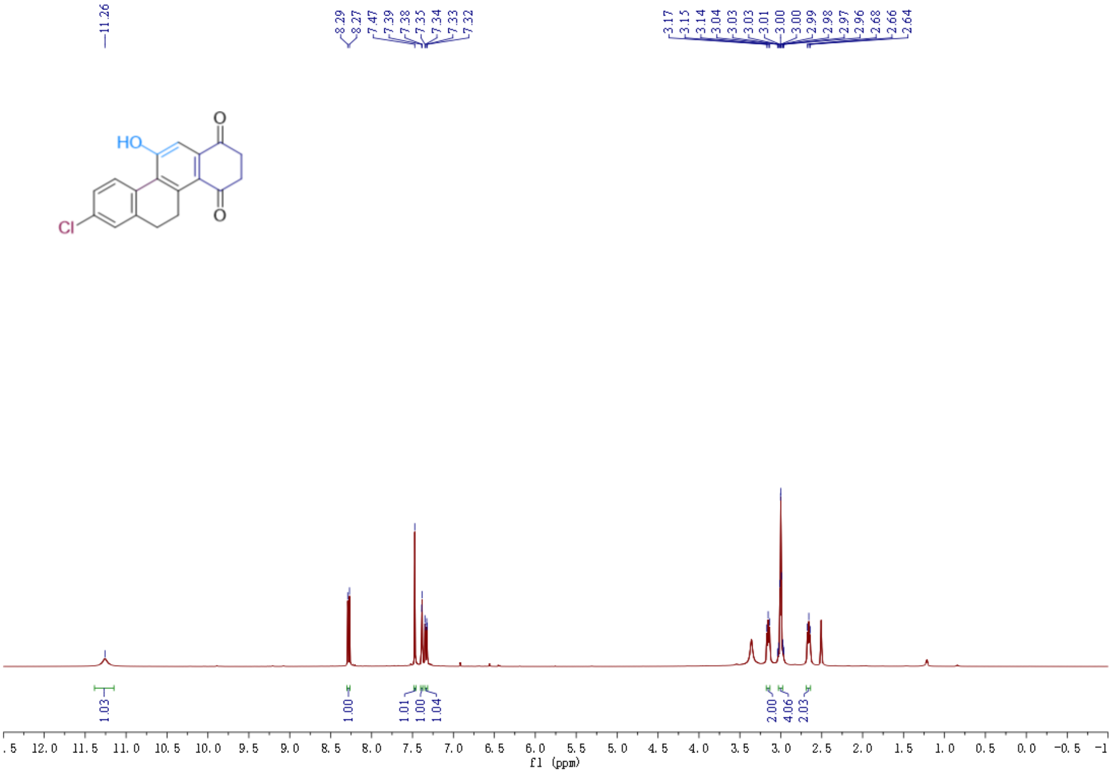

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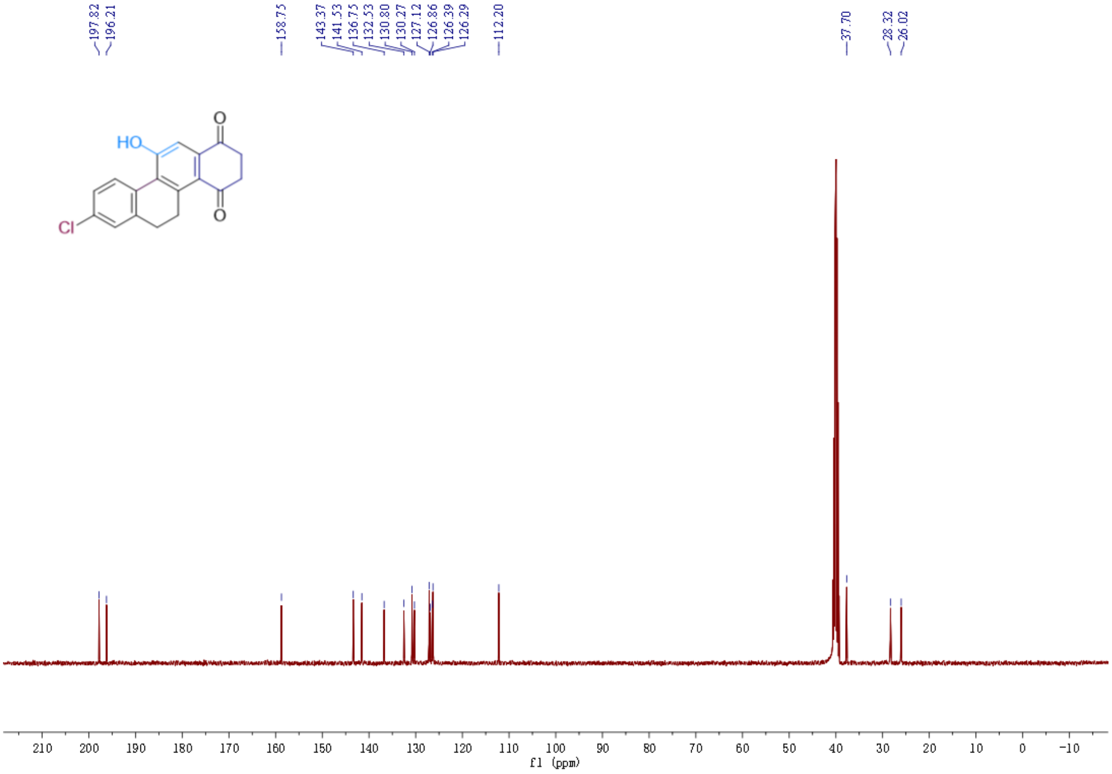

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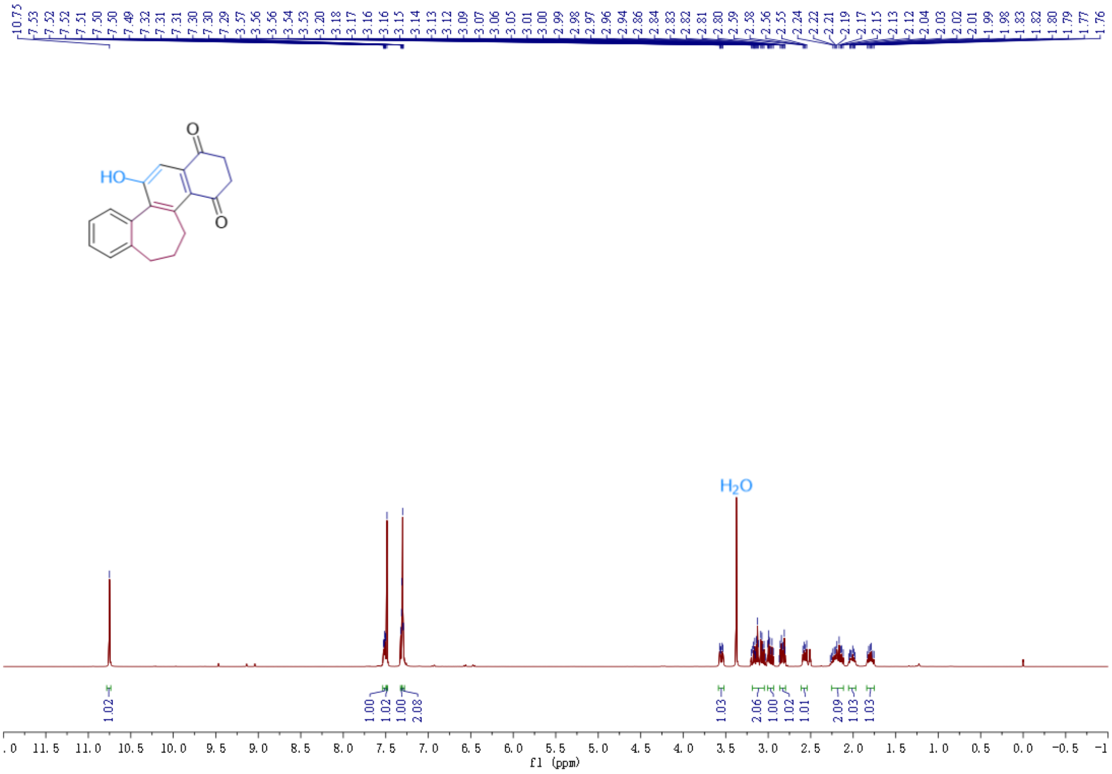
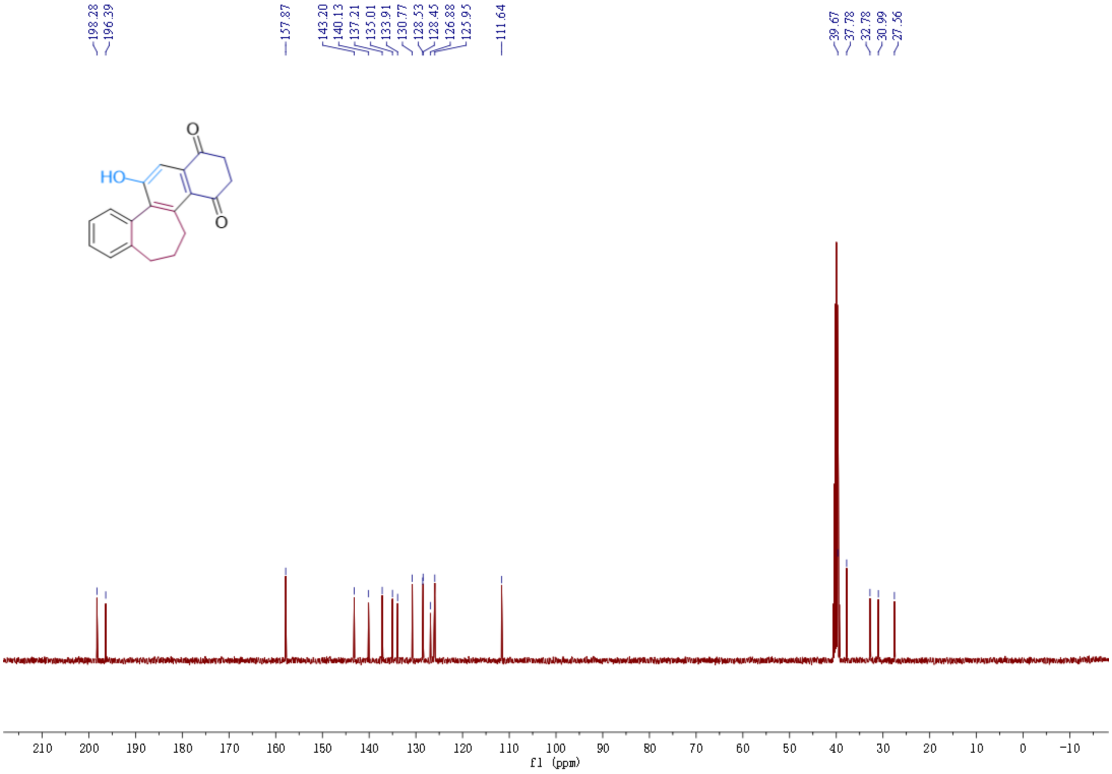


^{13}C NMR spectra of 6i (101 MHz, $(CD_3)_2SO$)



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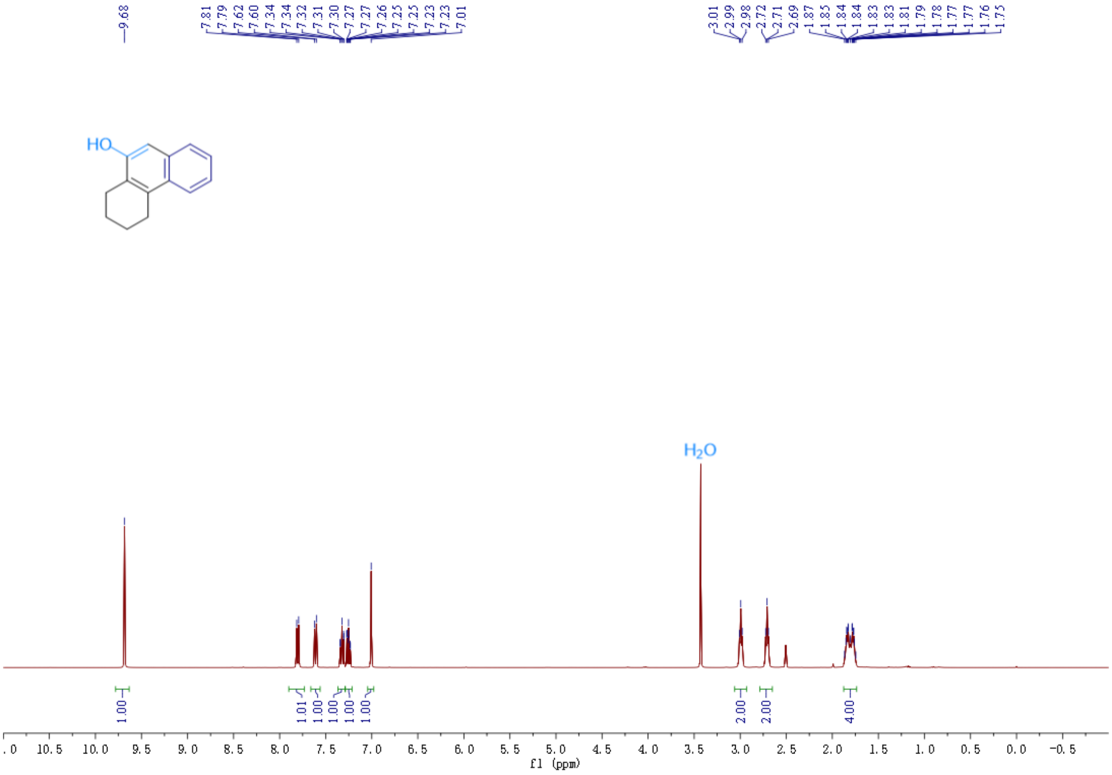

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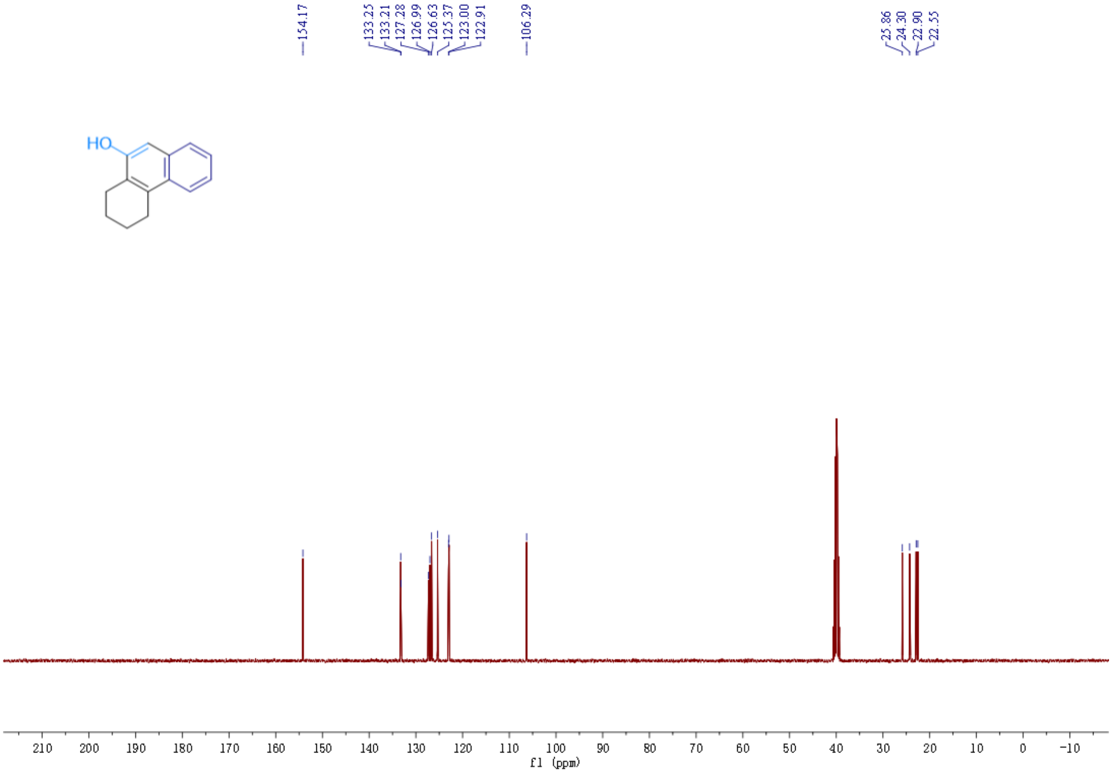

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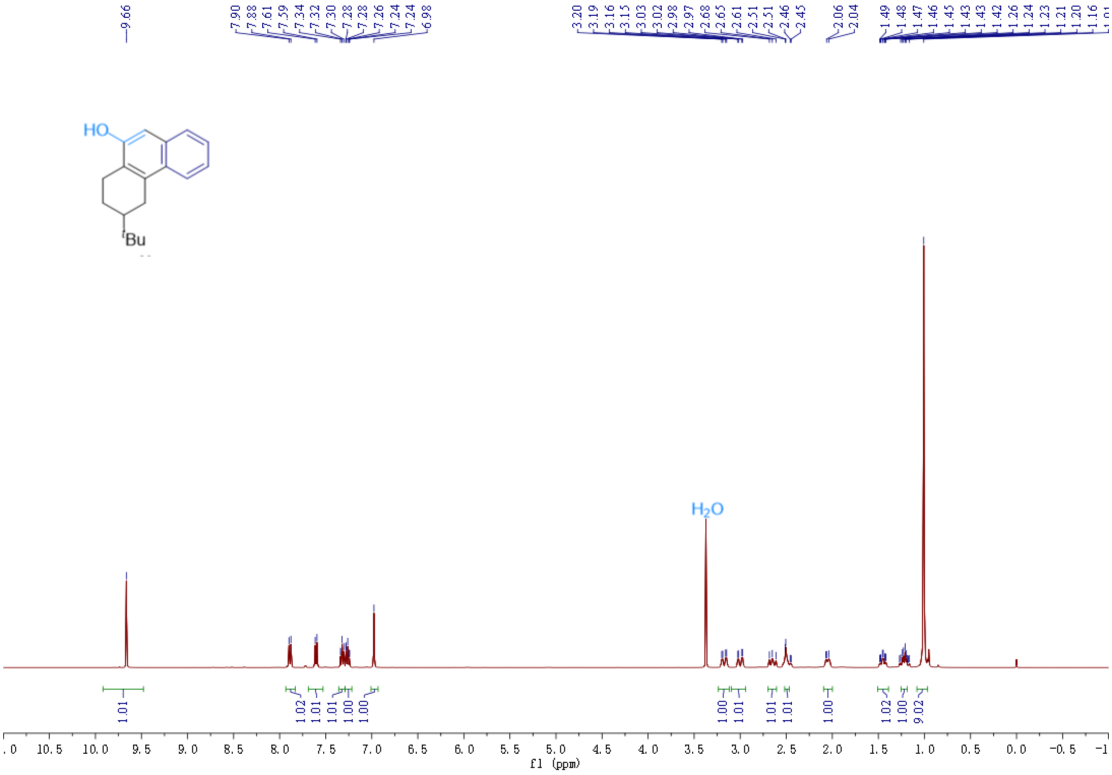

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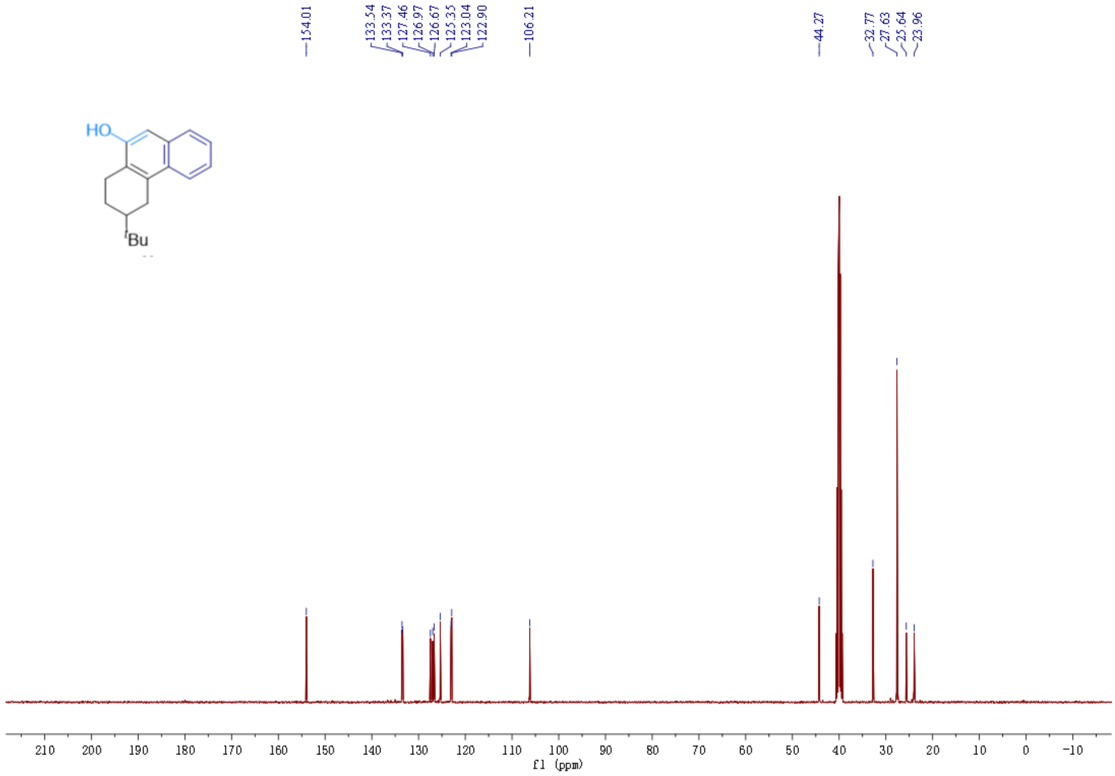

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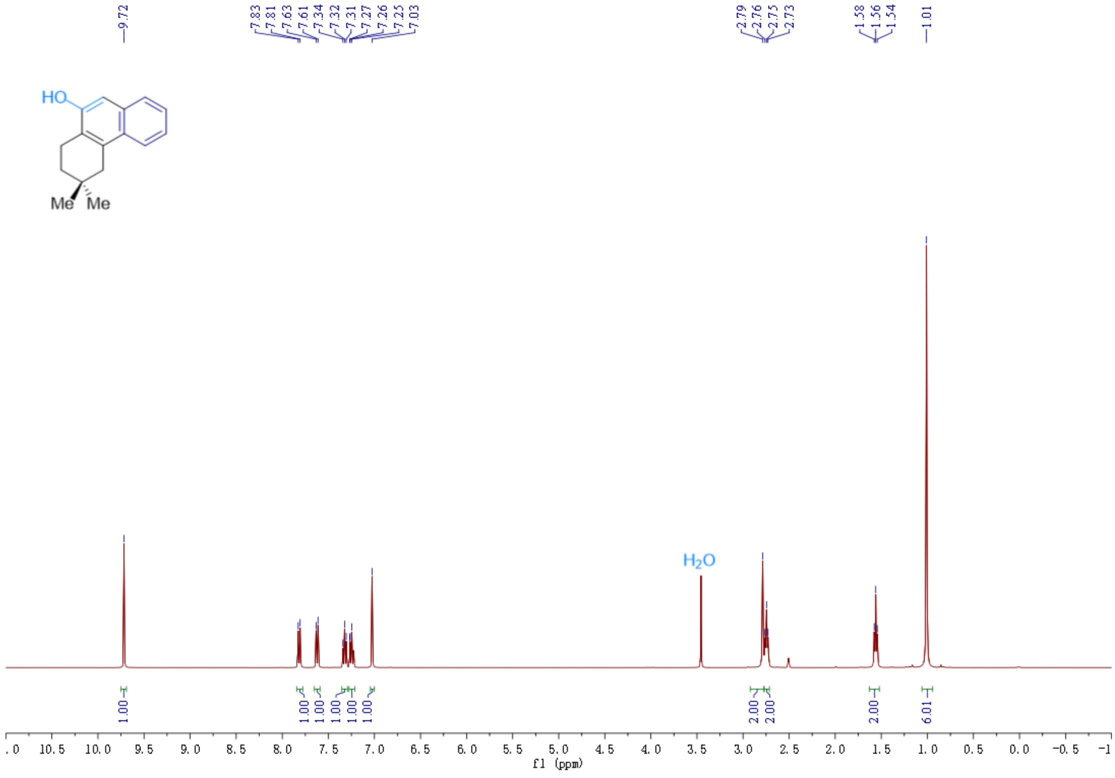

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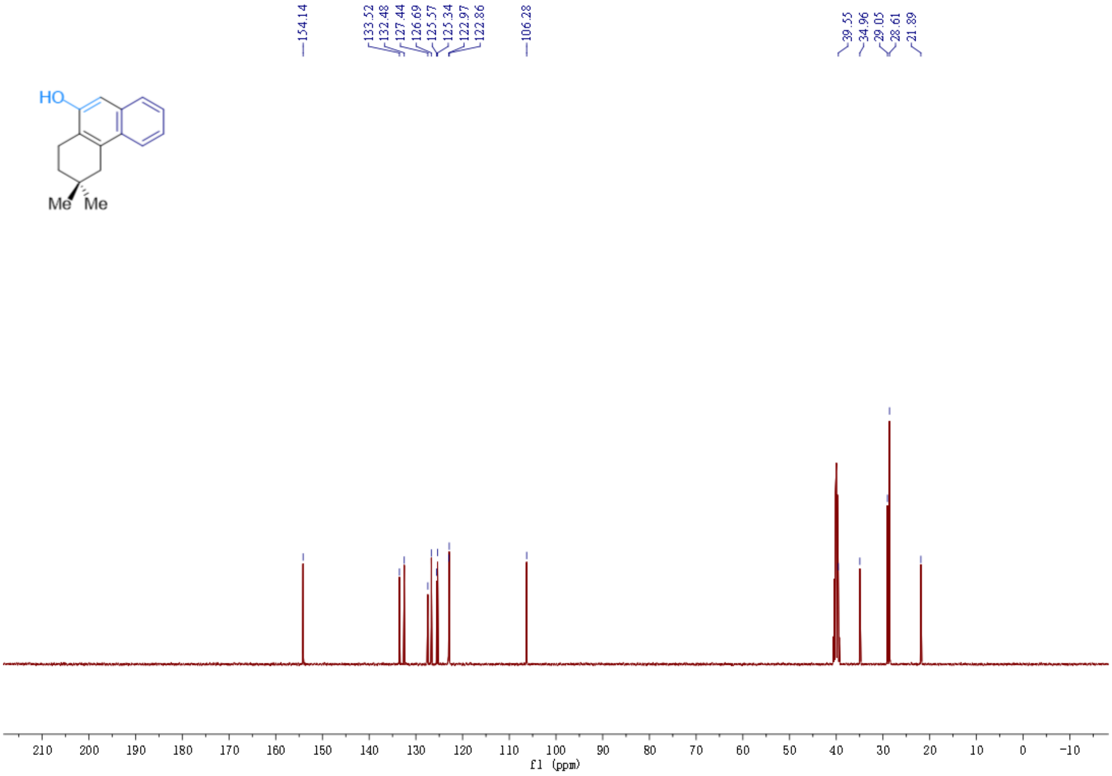

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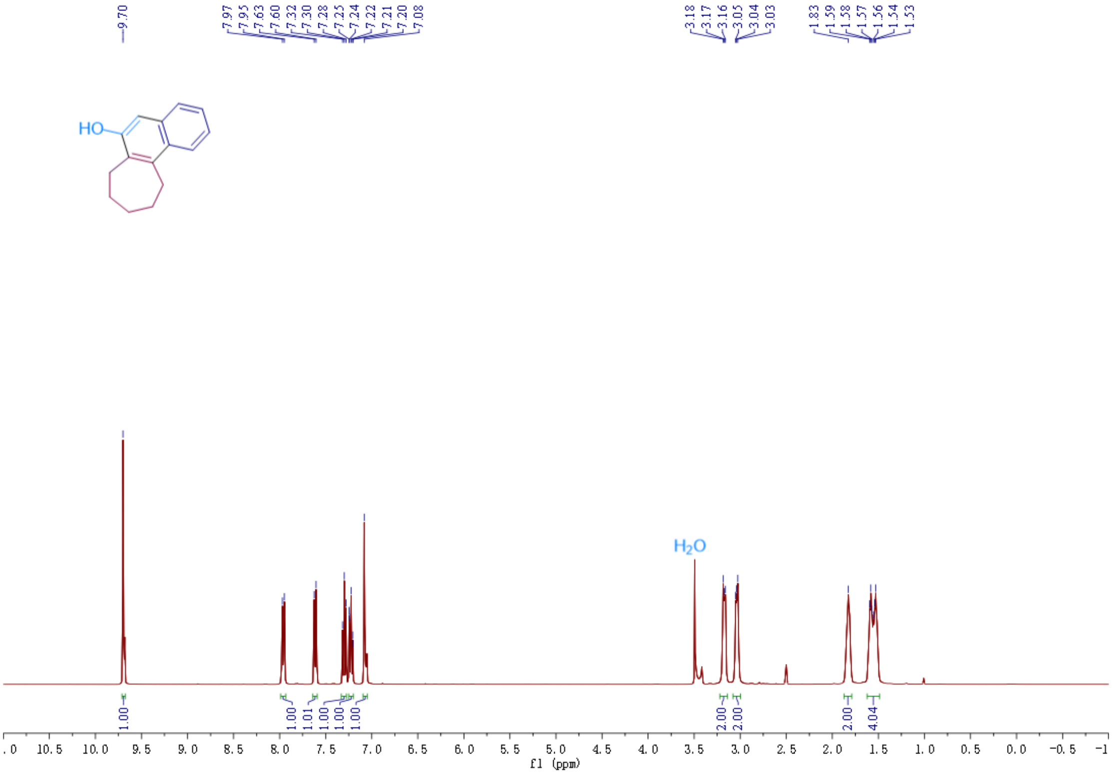

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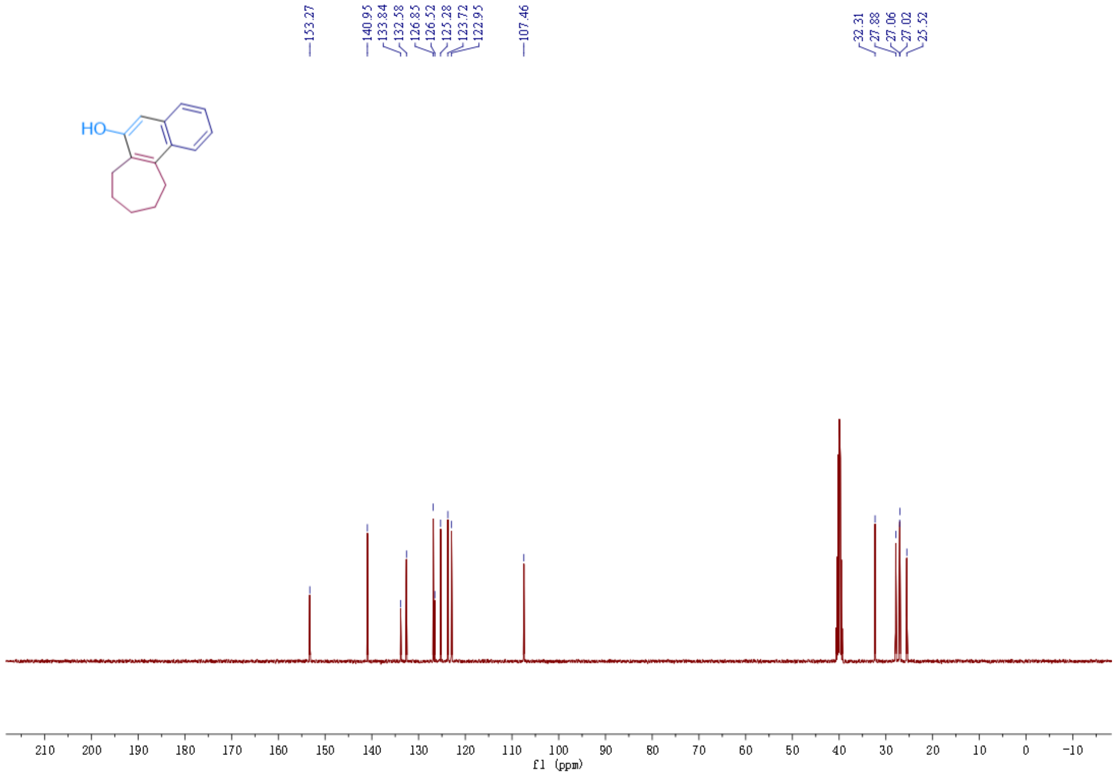

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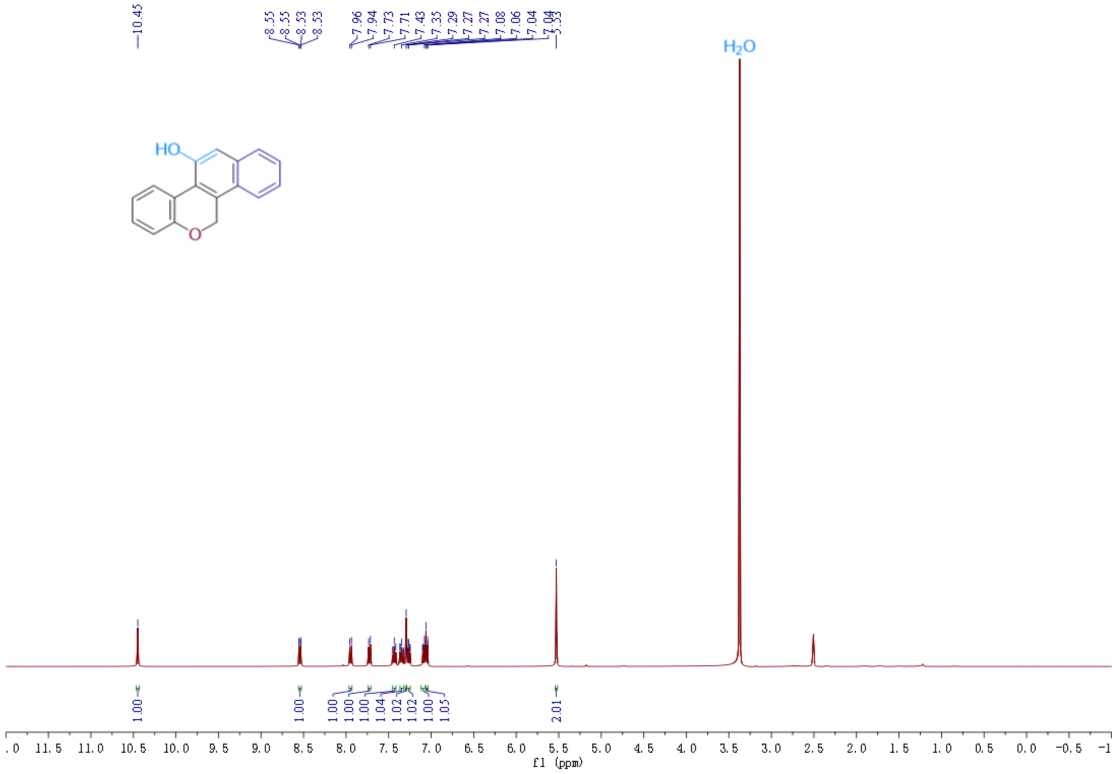

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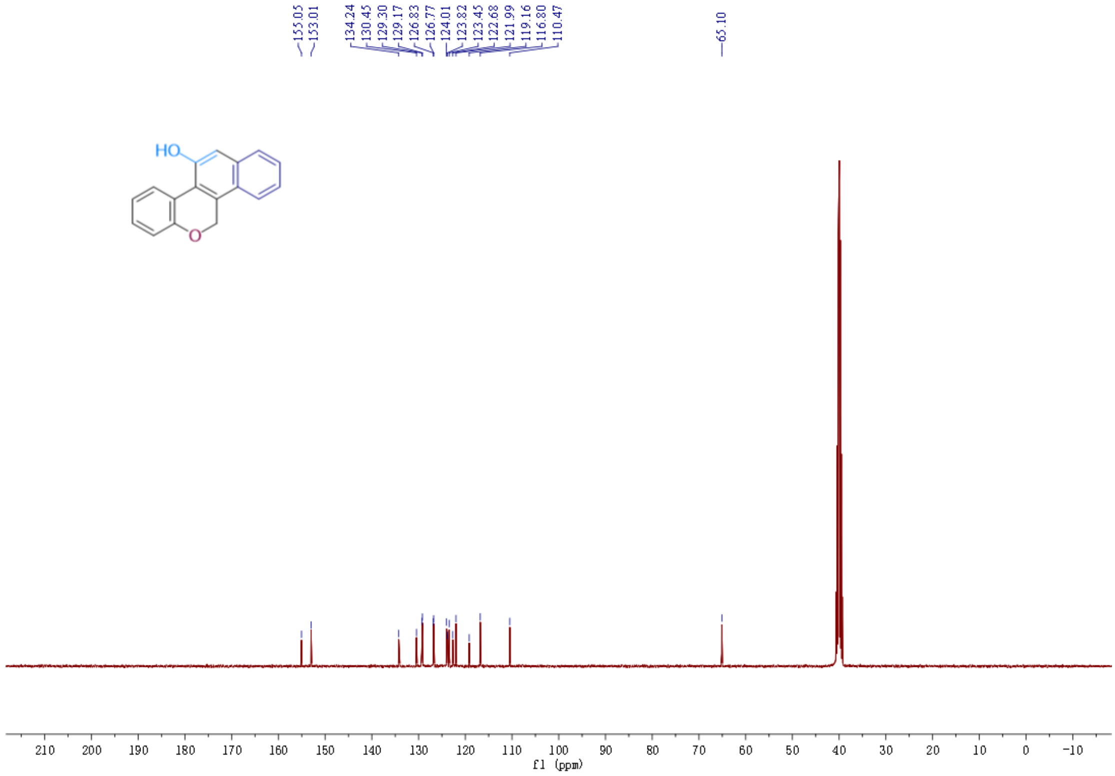

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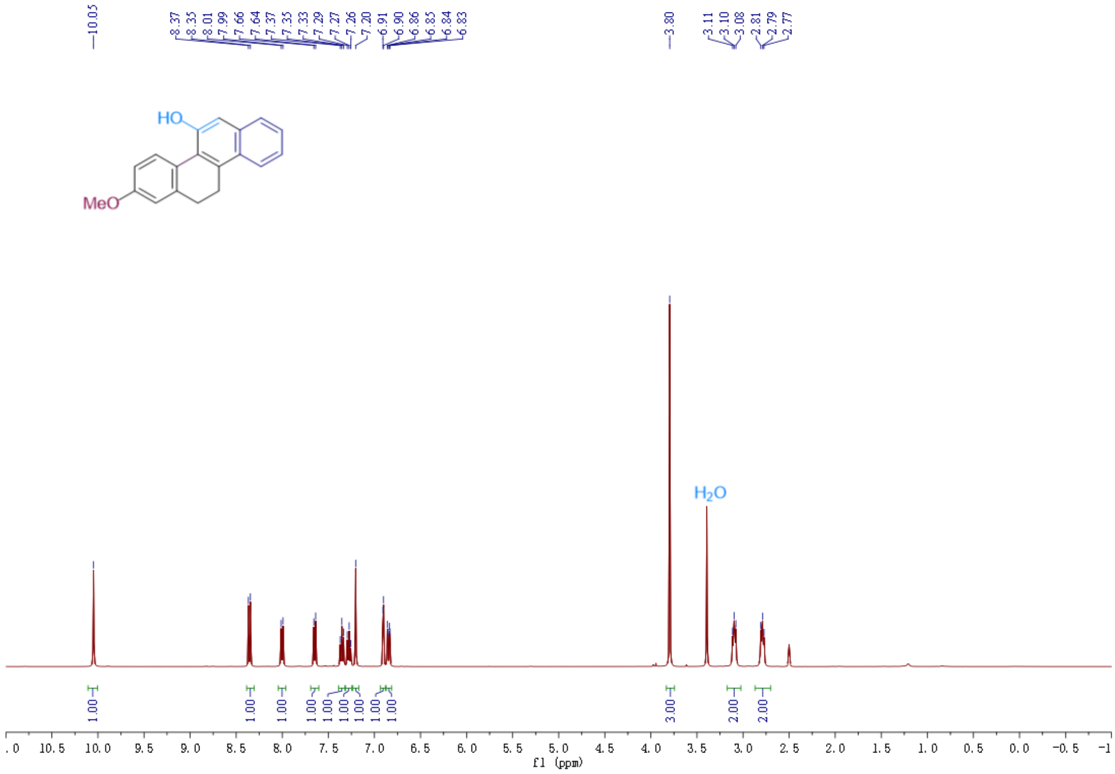

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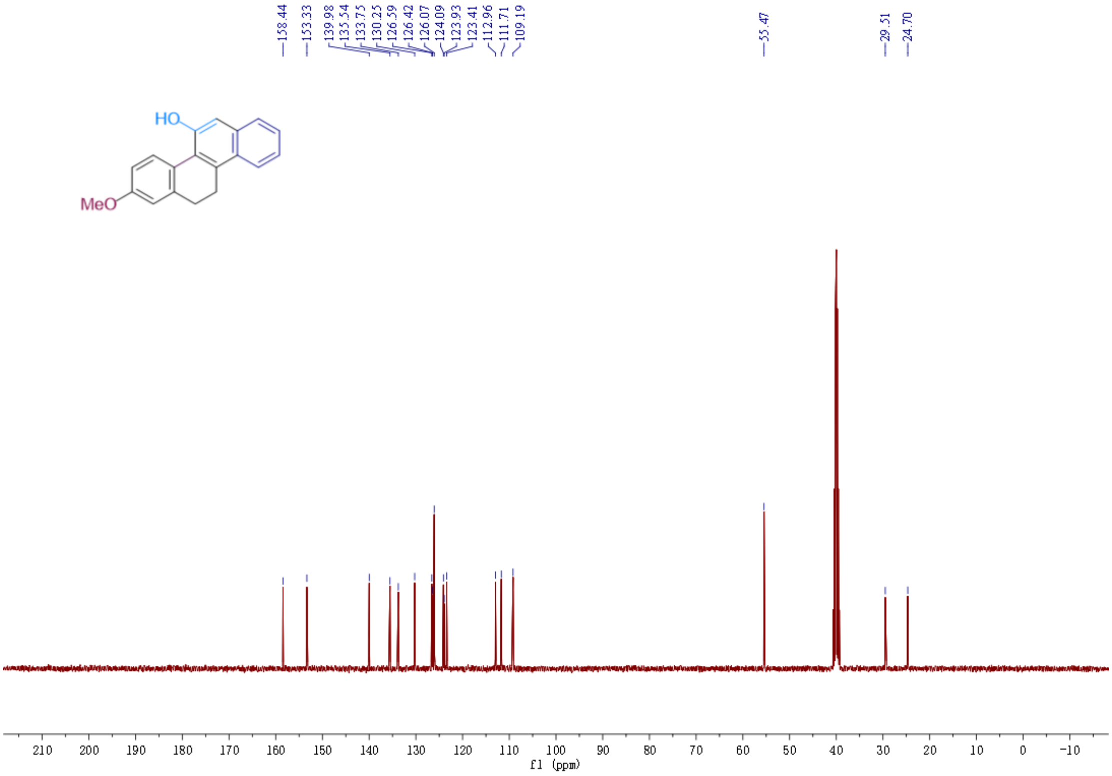

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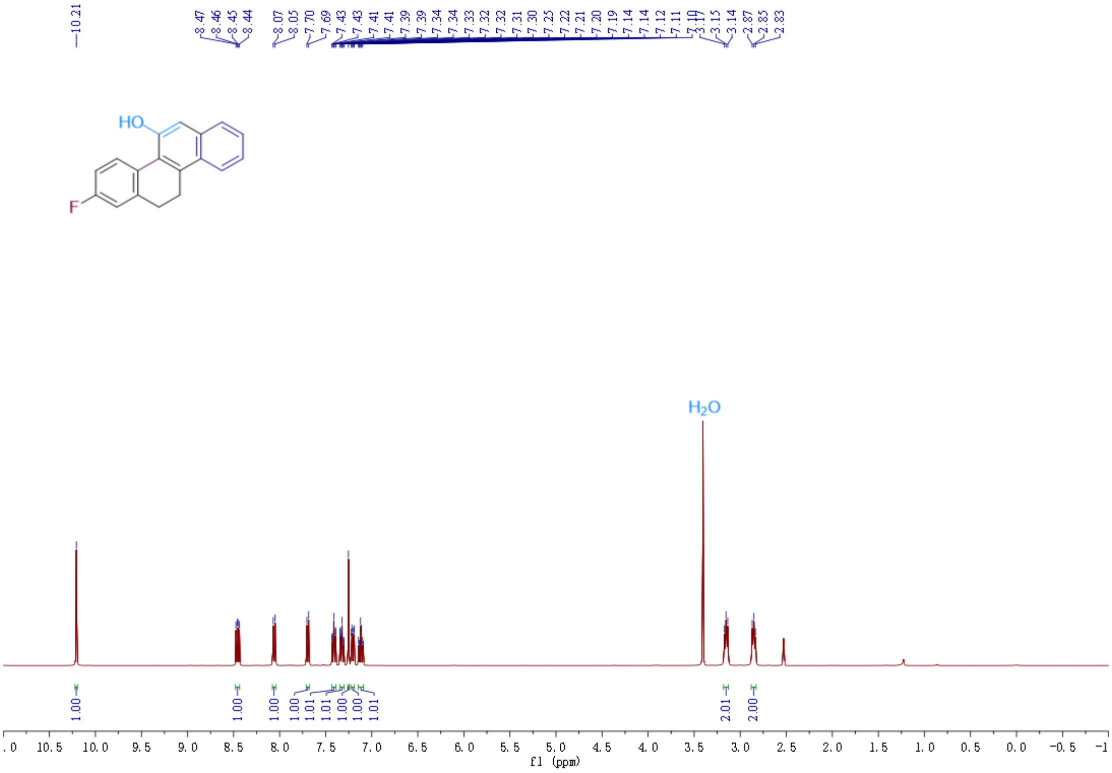

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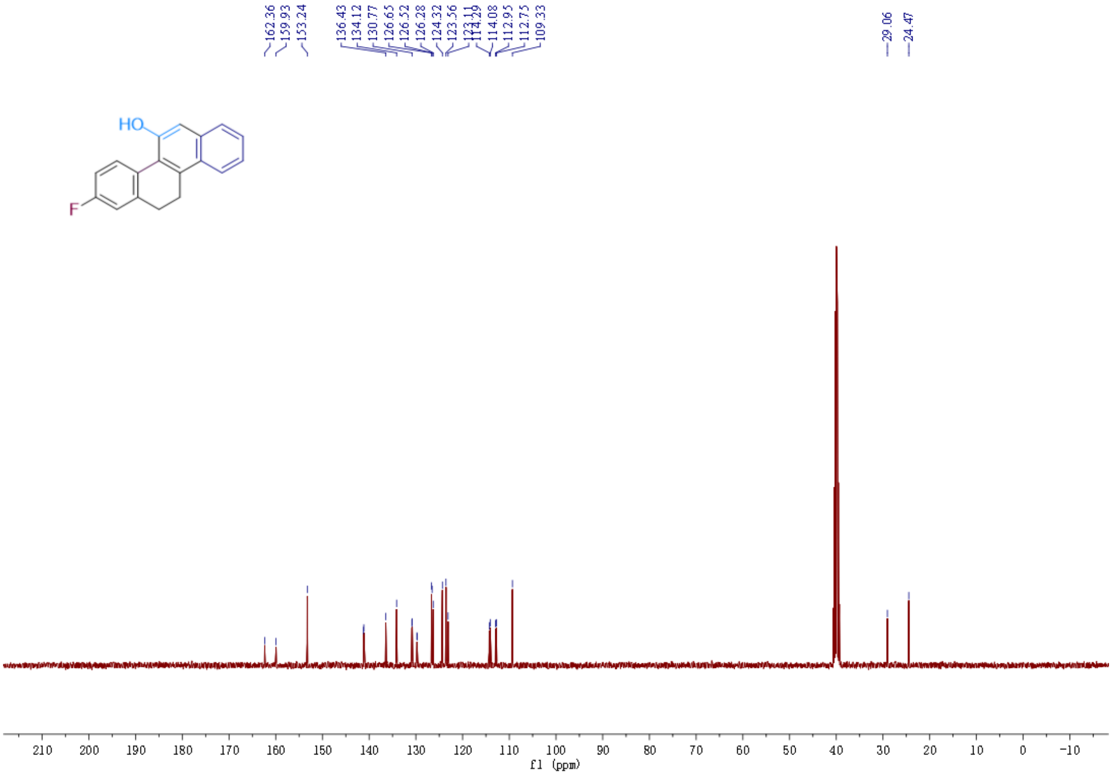
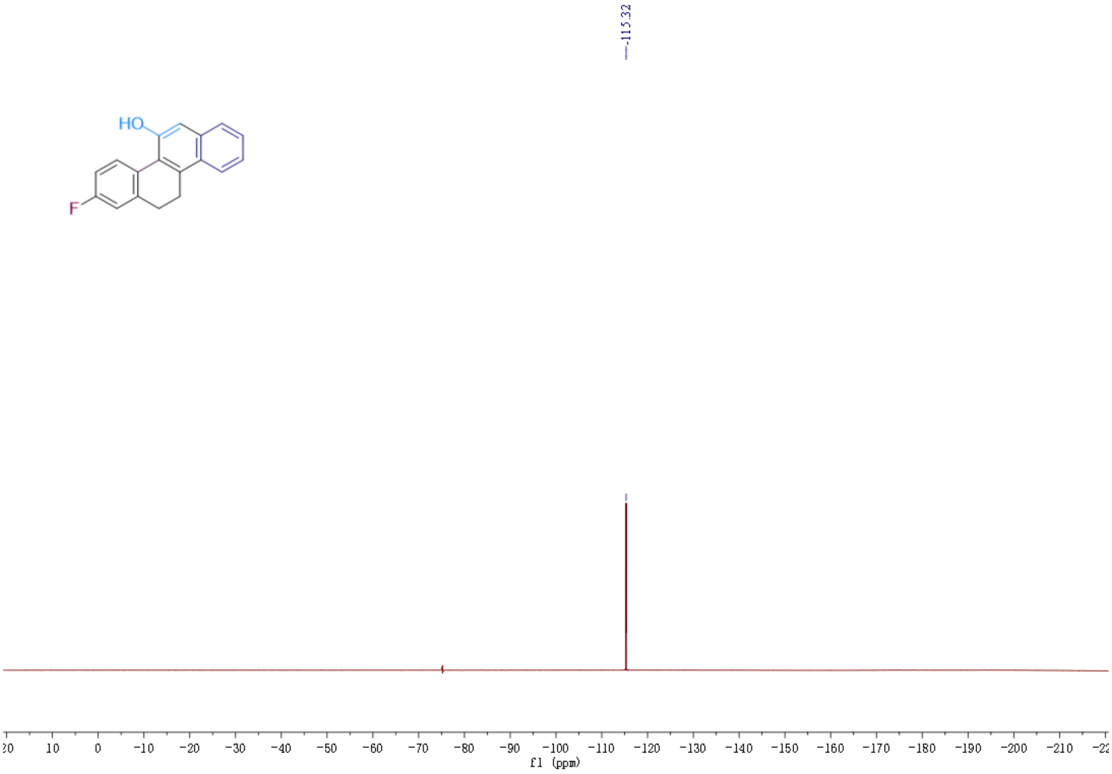


^{19}F NMR NMR spectra of 7g (377 MHz, $(CD_3)_2SO$)



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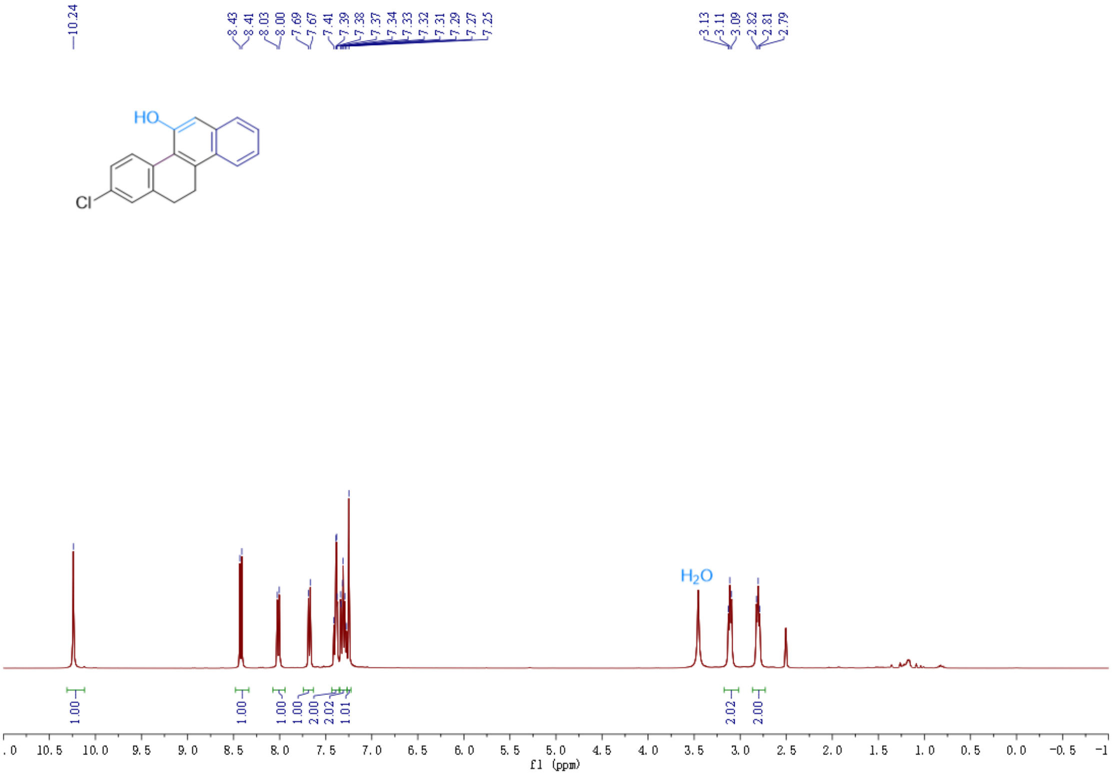

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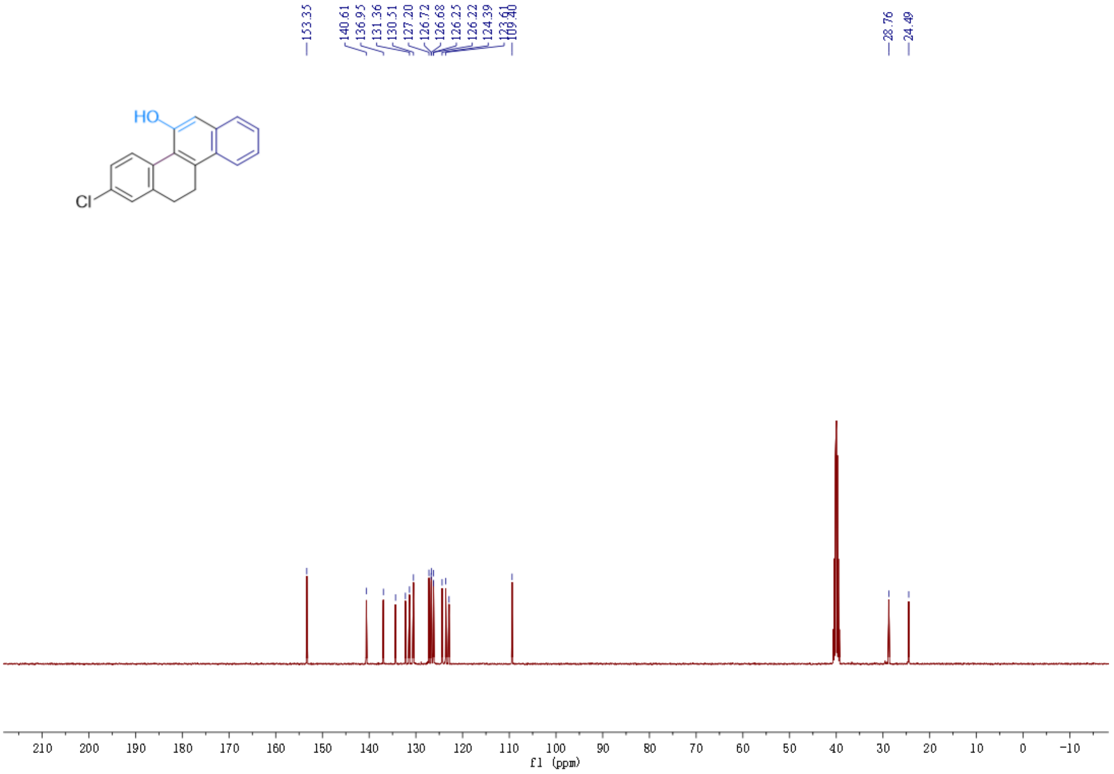

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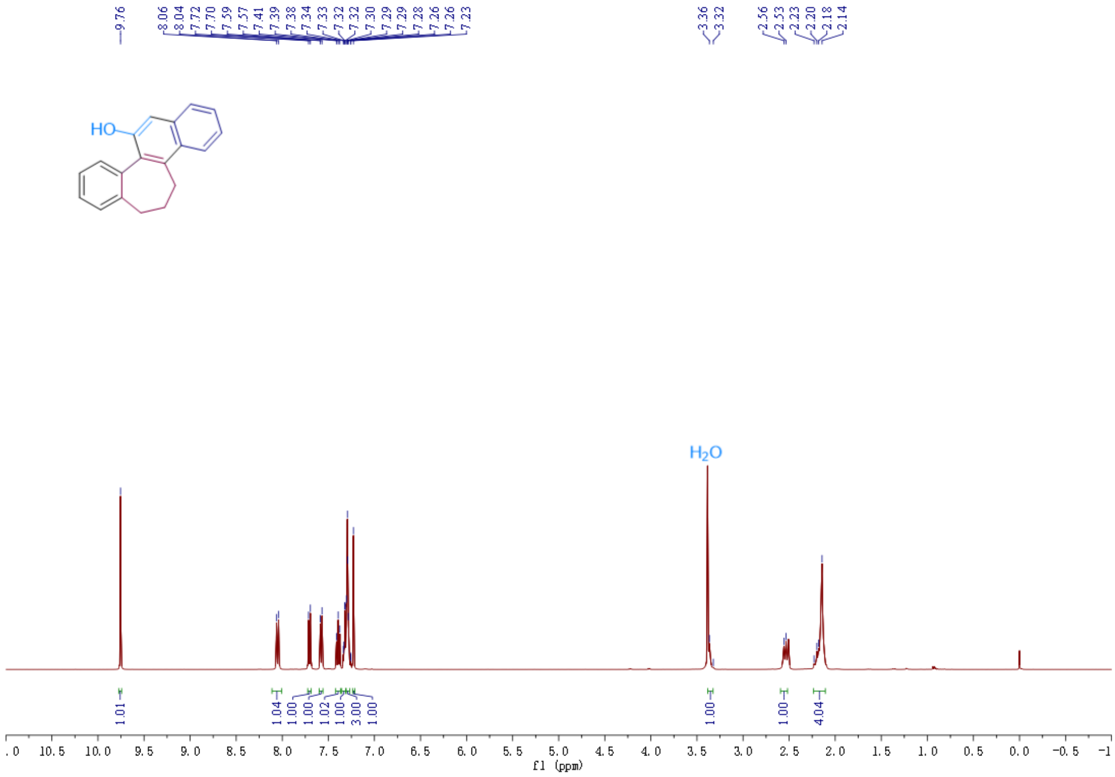

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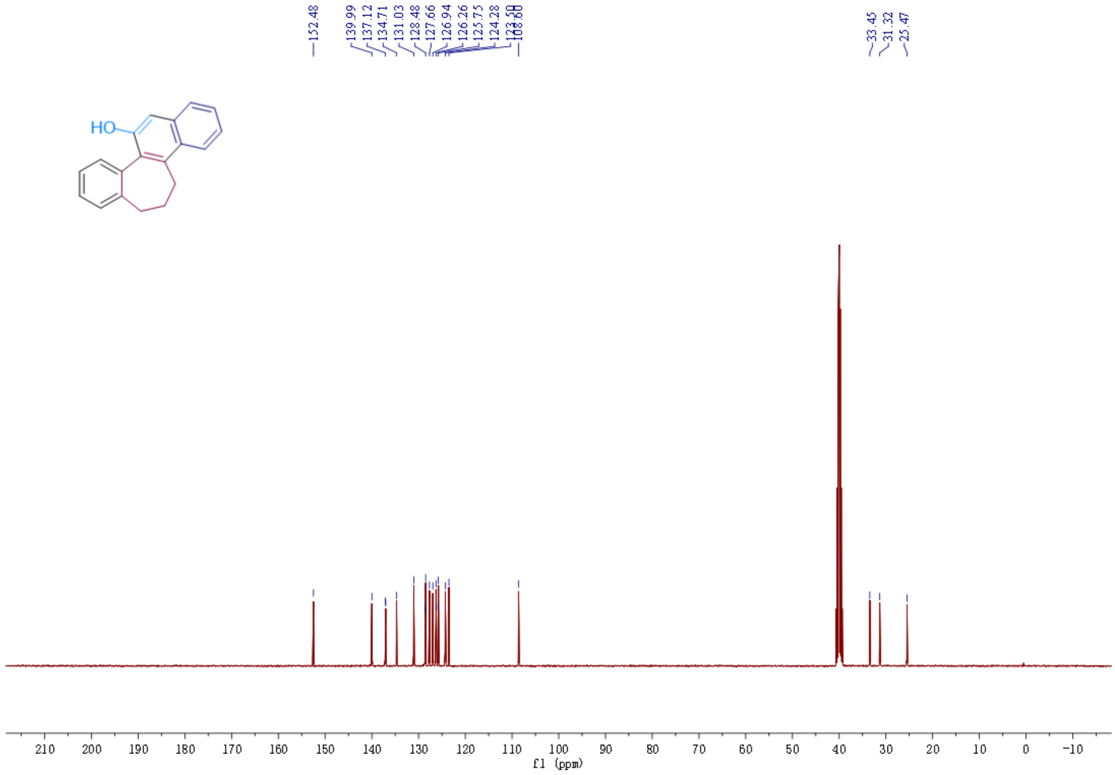

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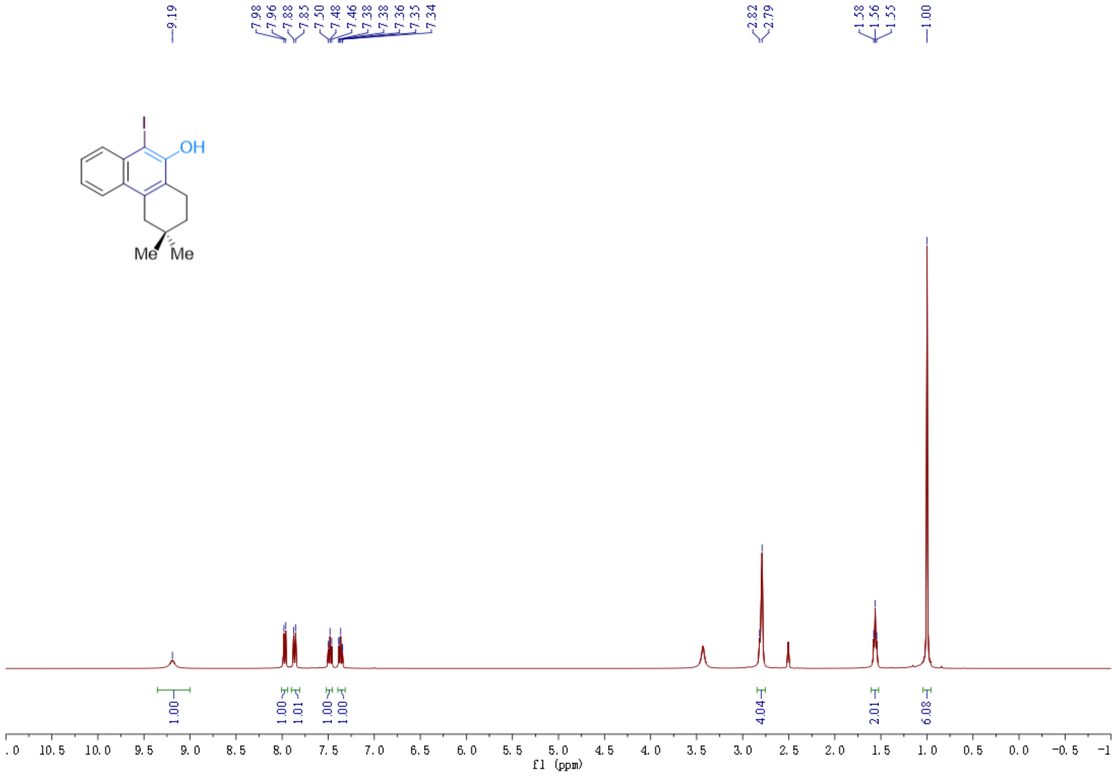

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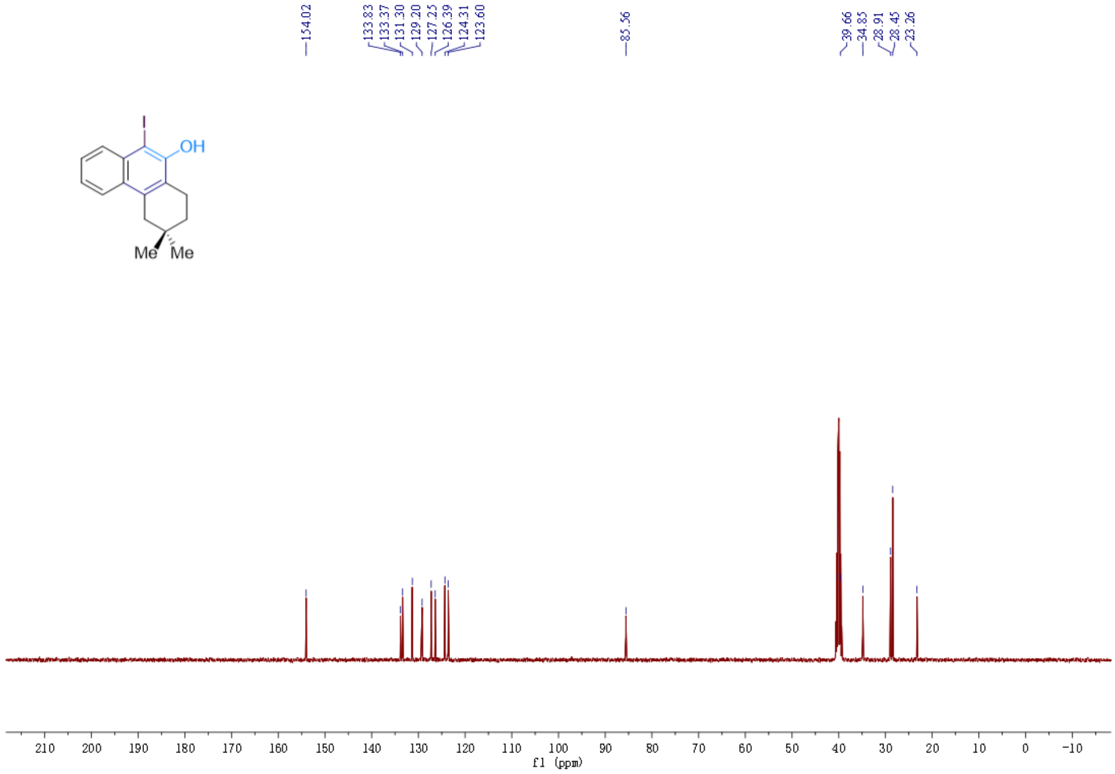

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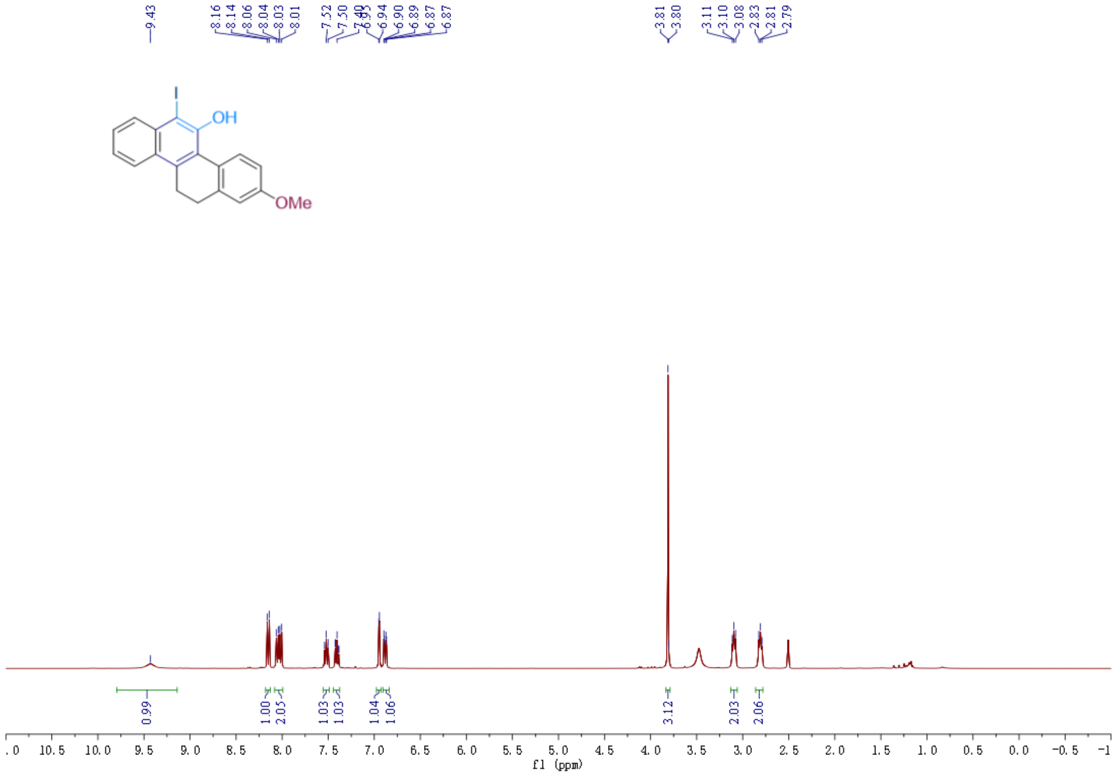

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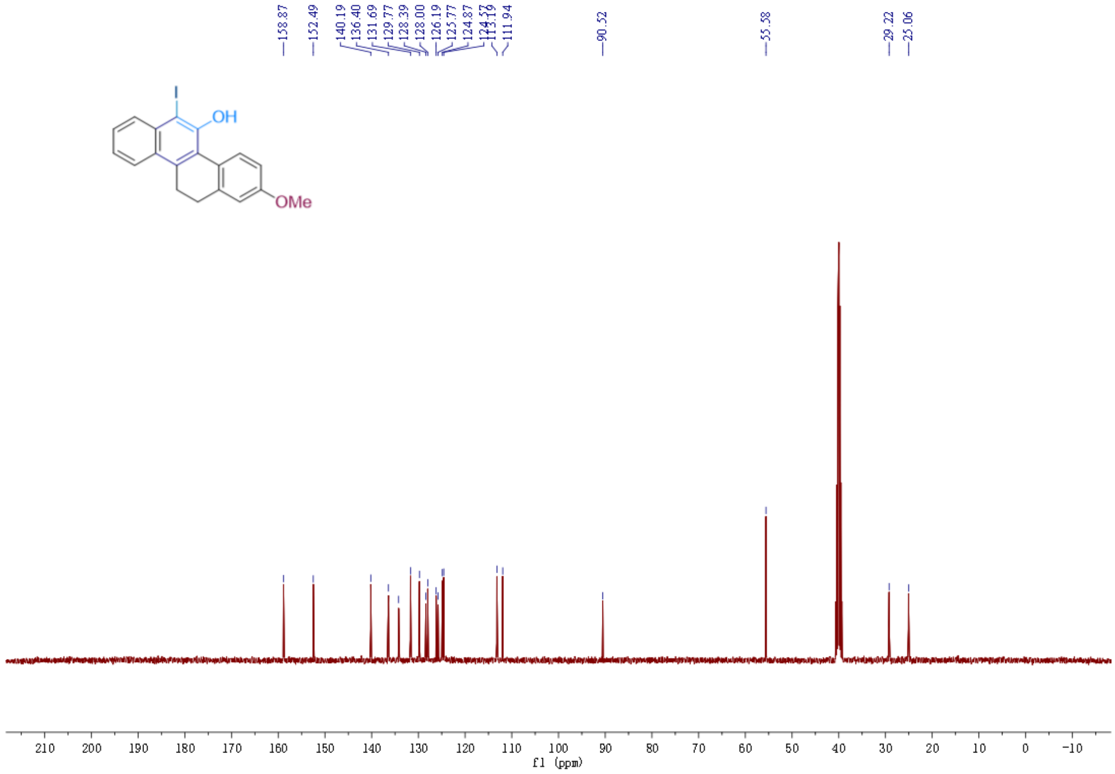

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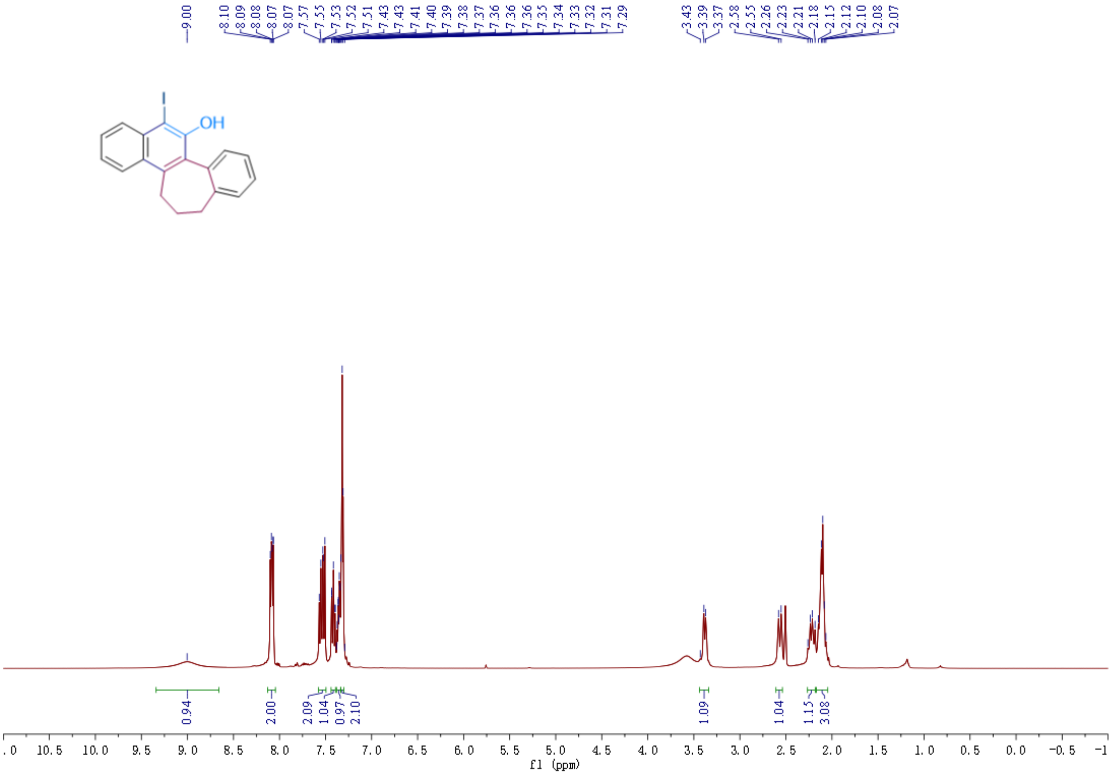

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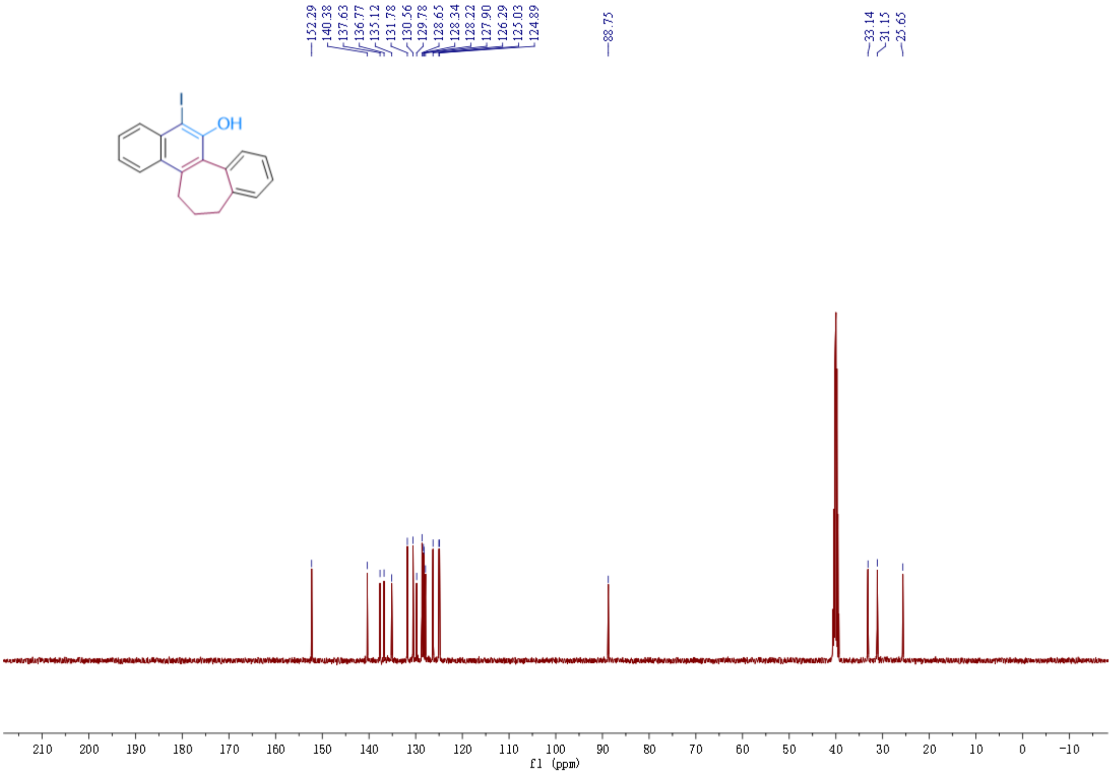

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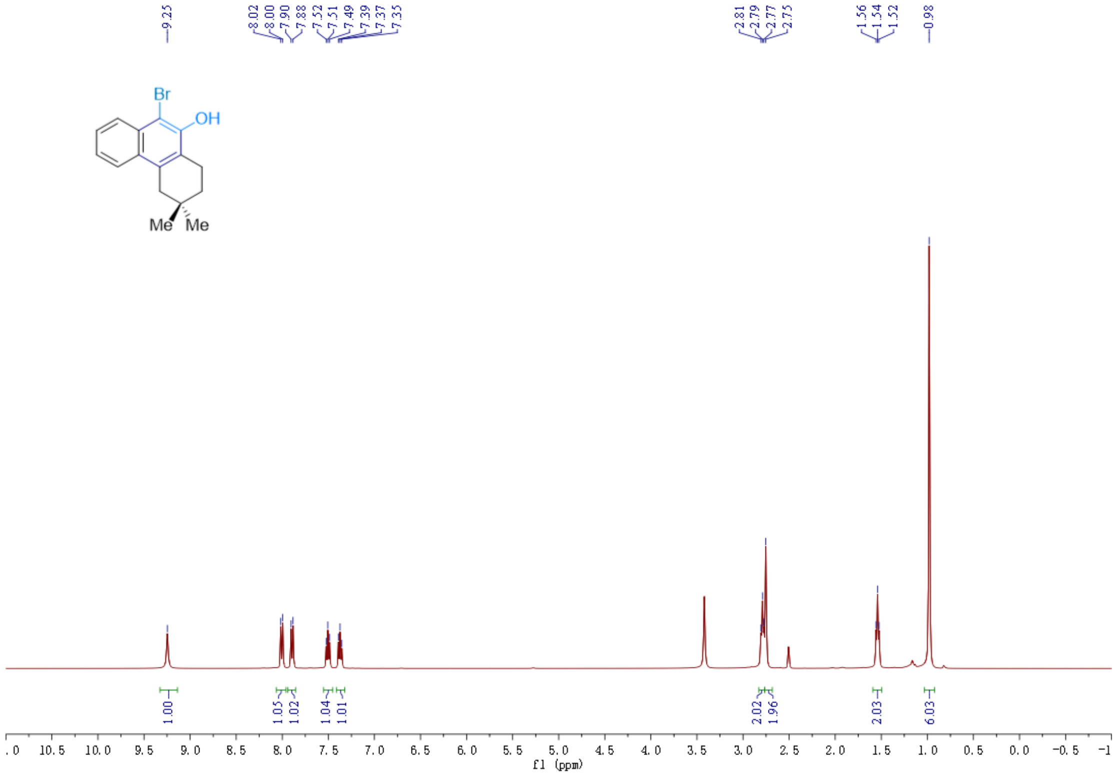

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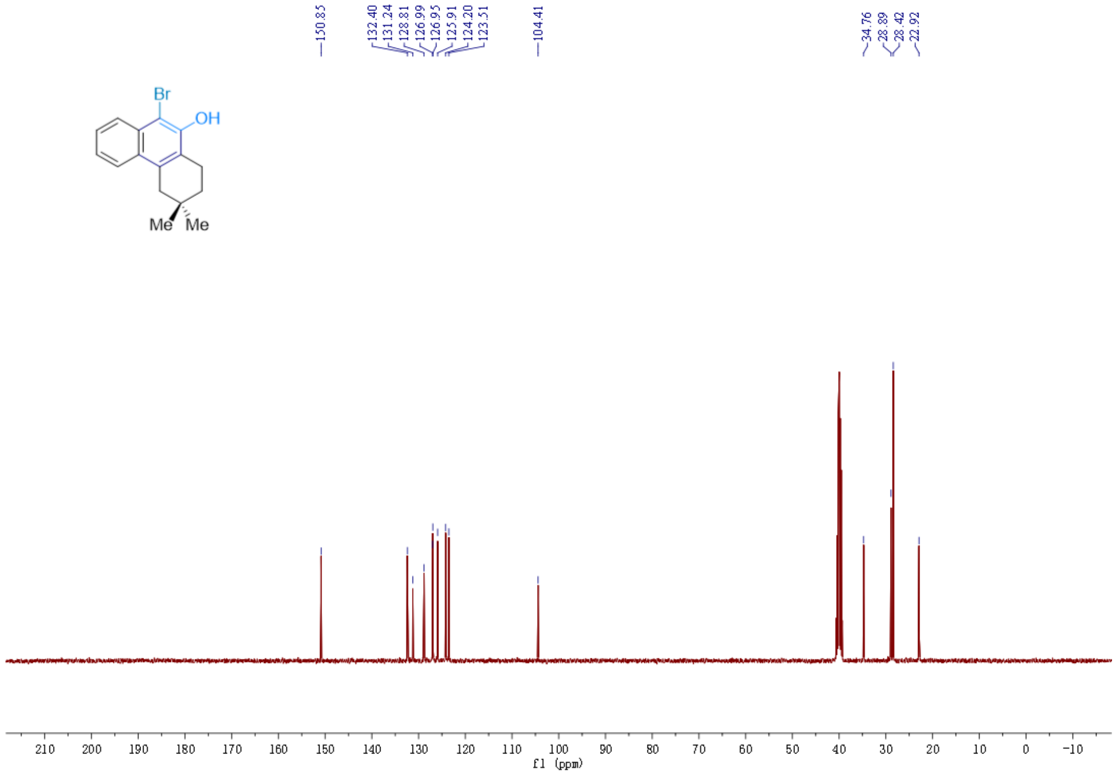

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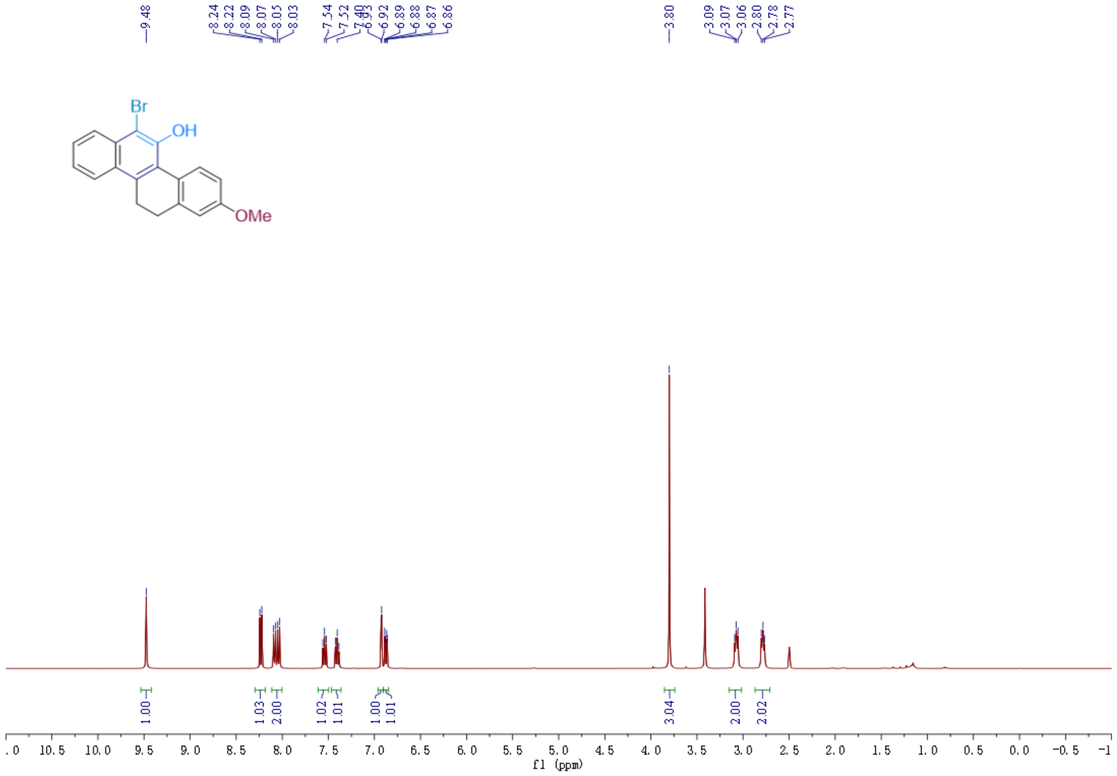

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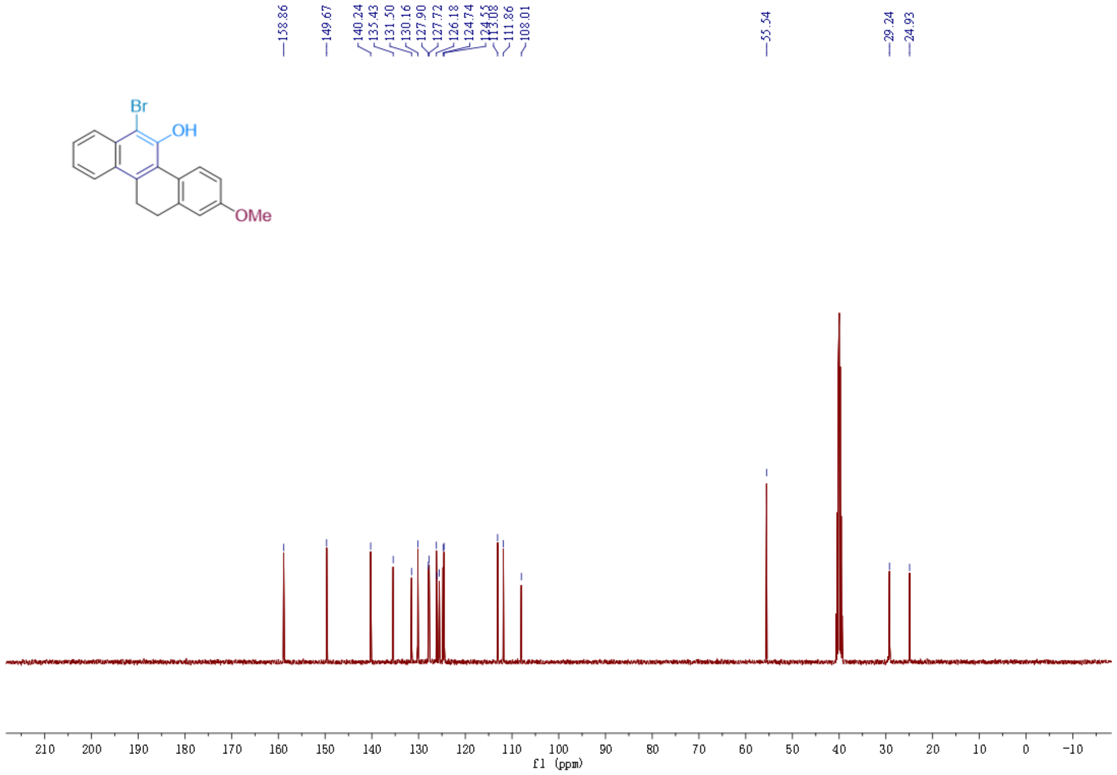

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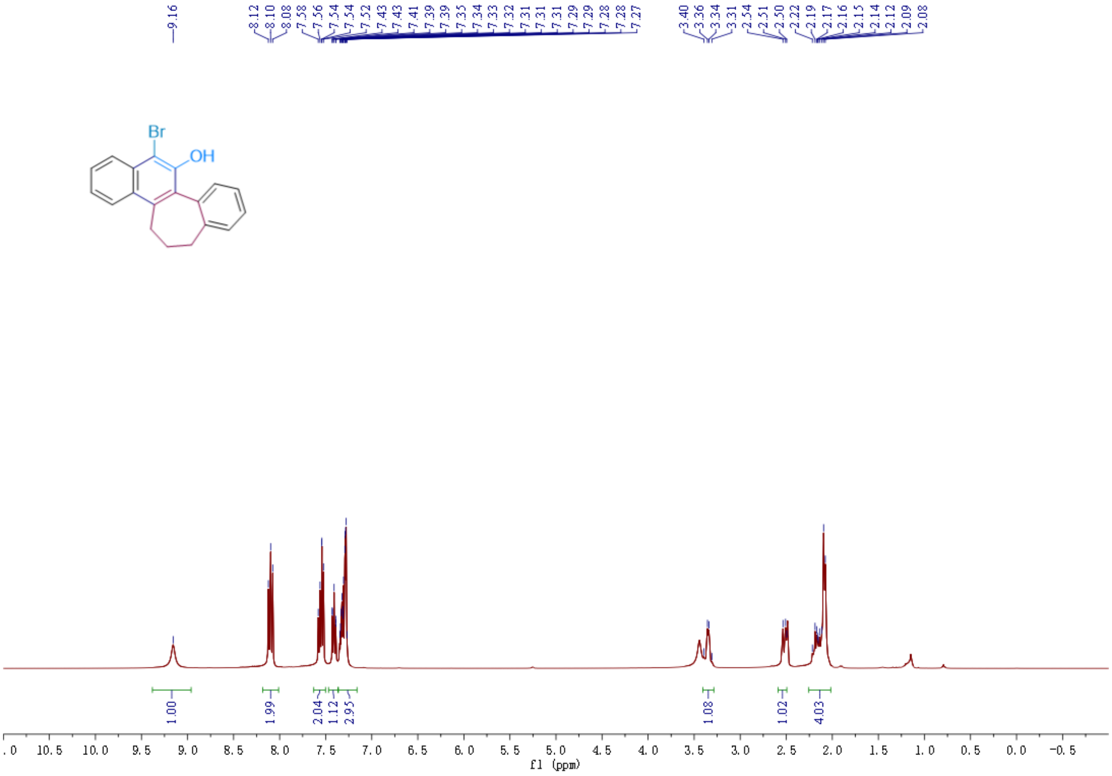

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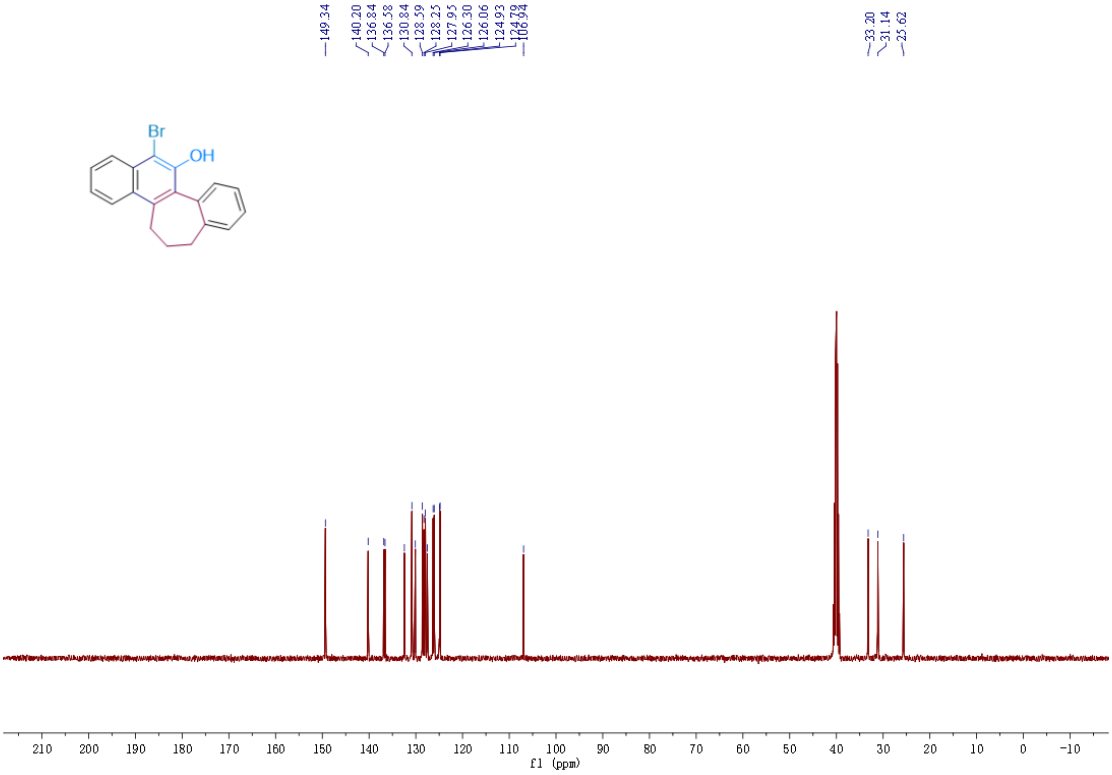

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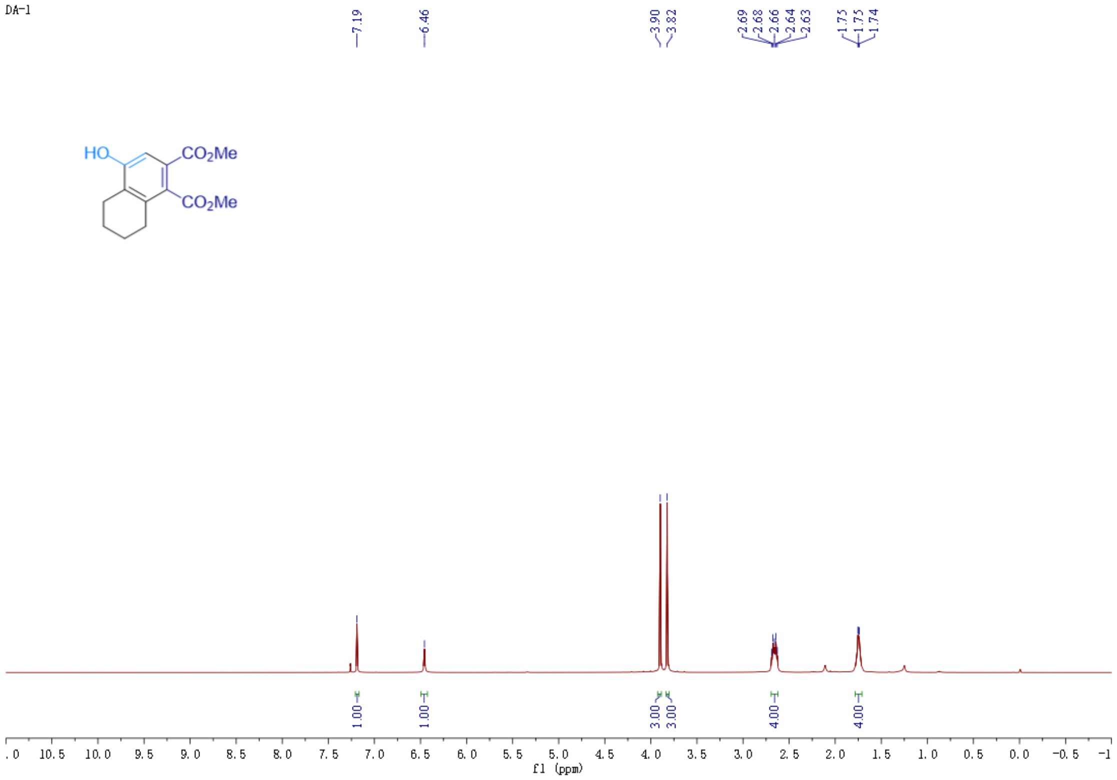

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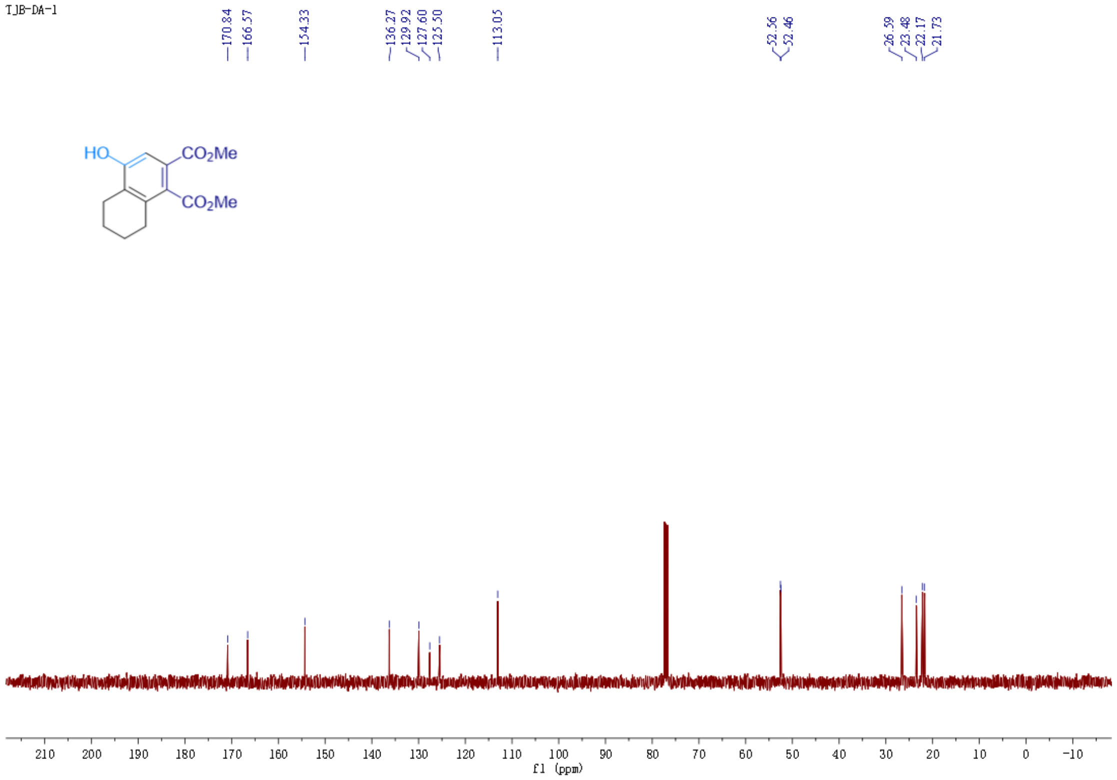

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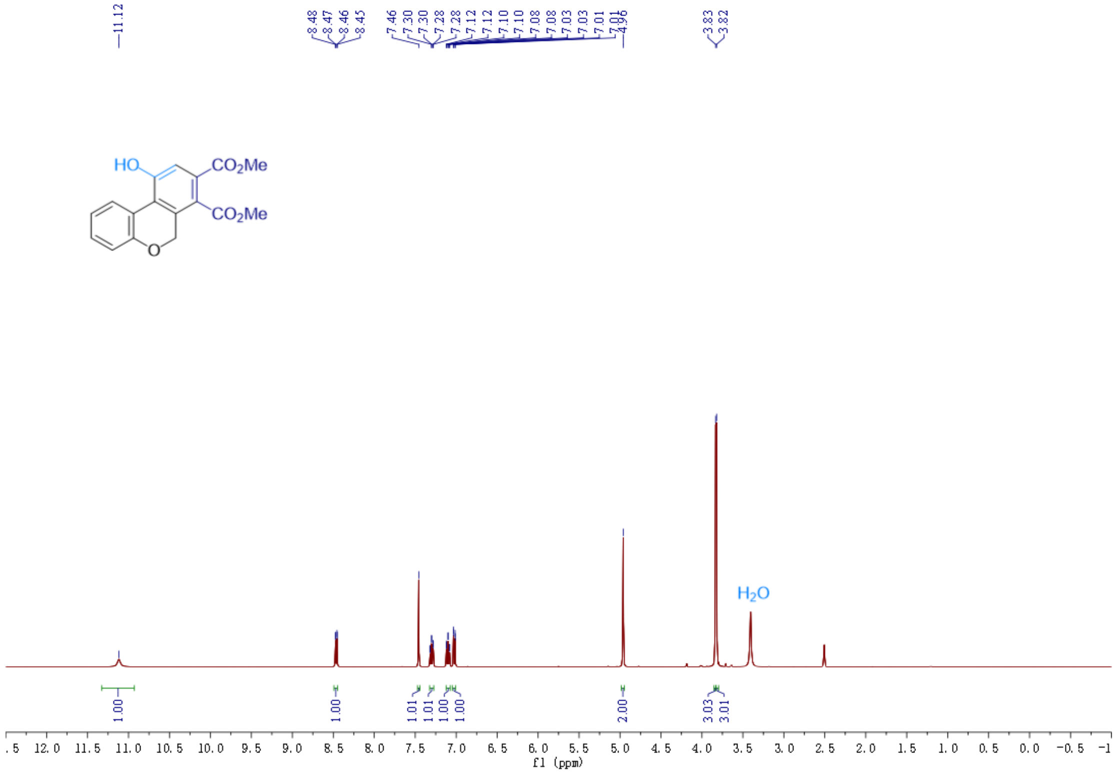

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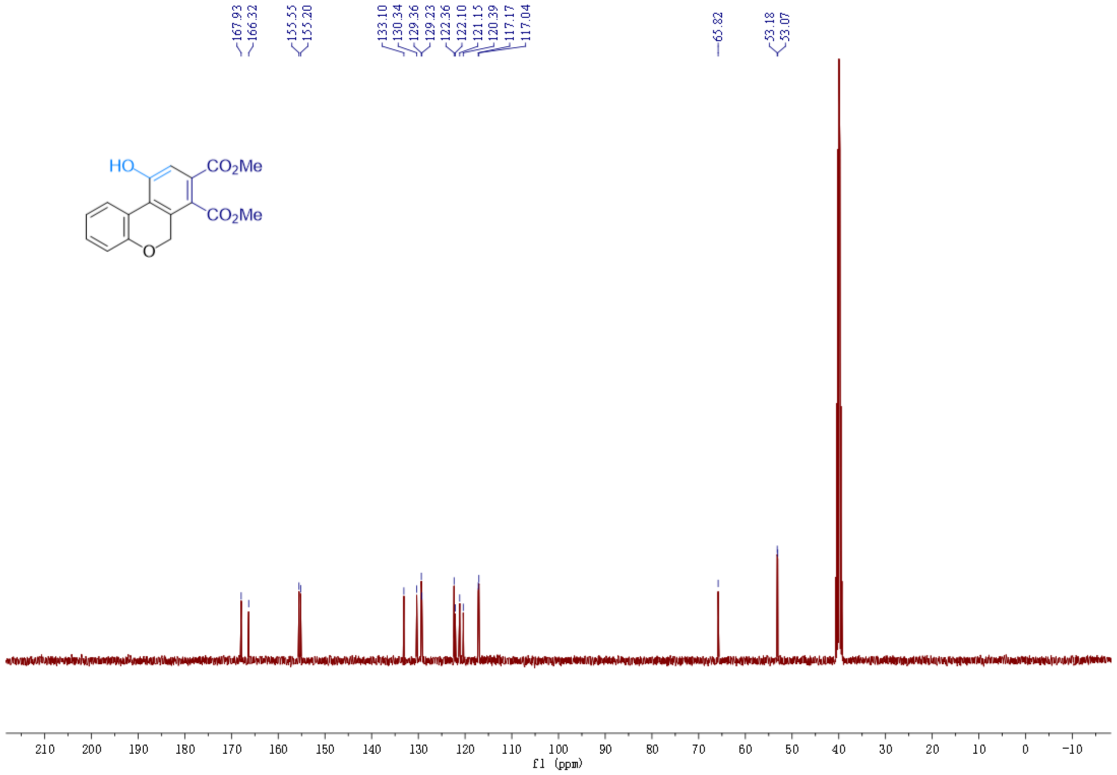

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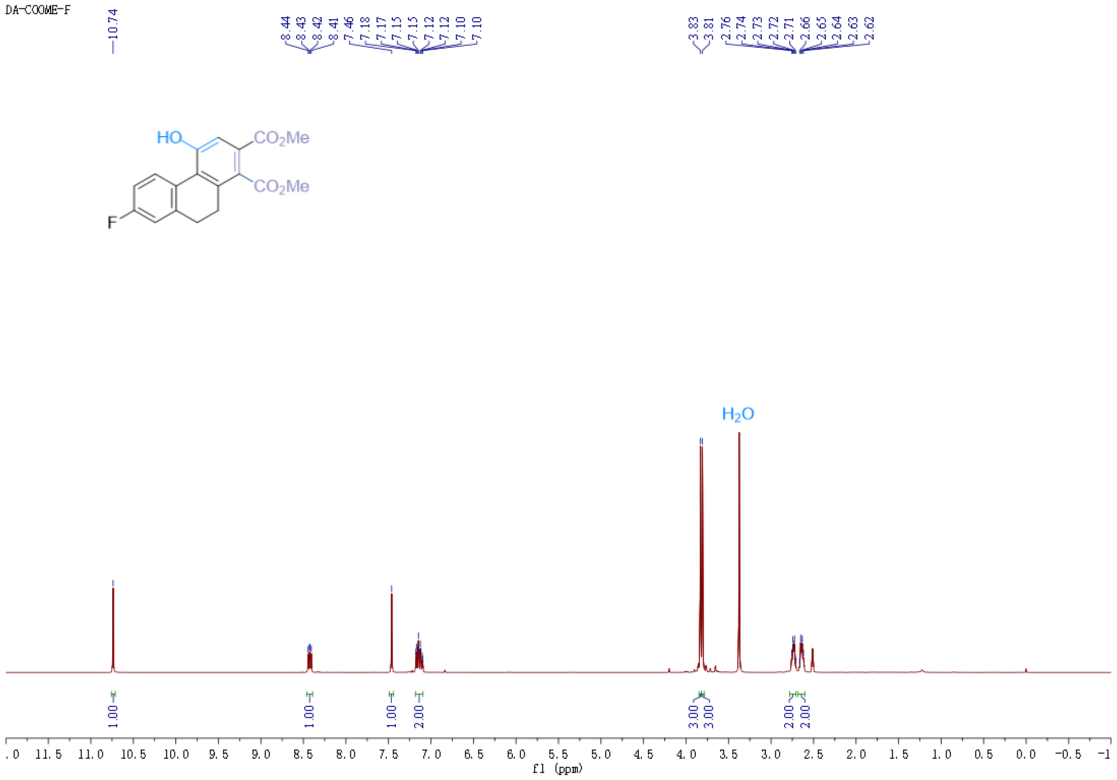
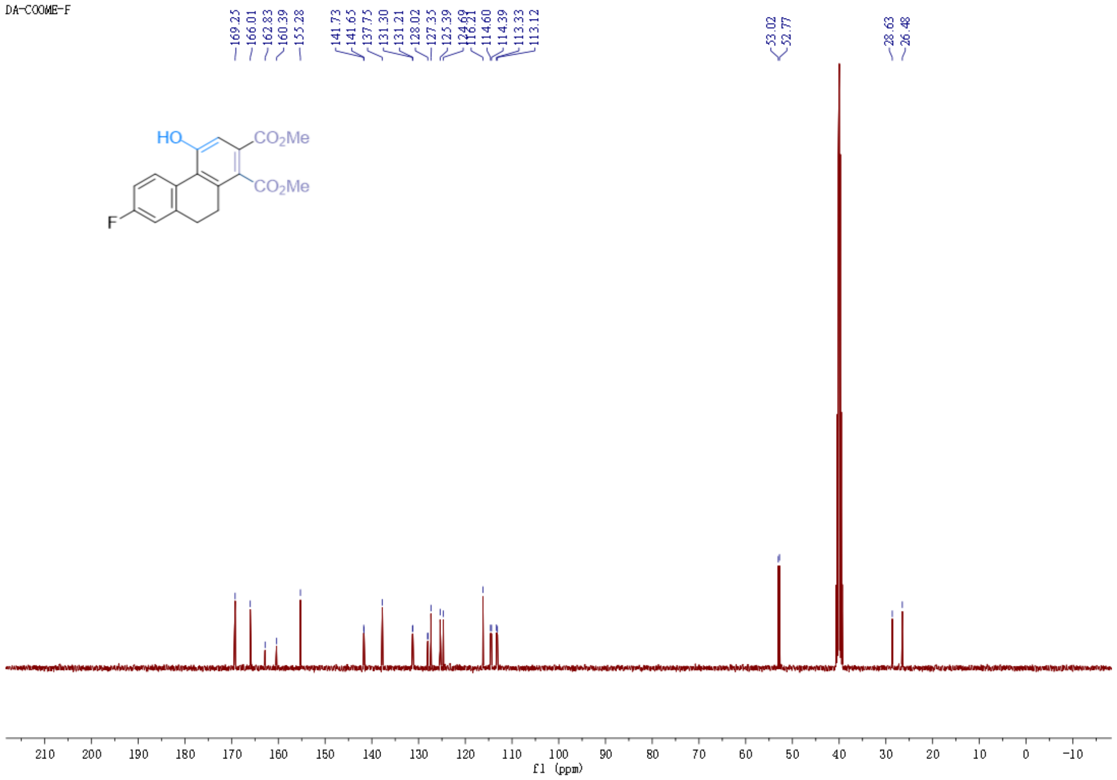
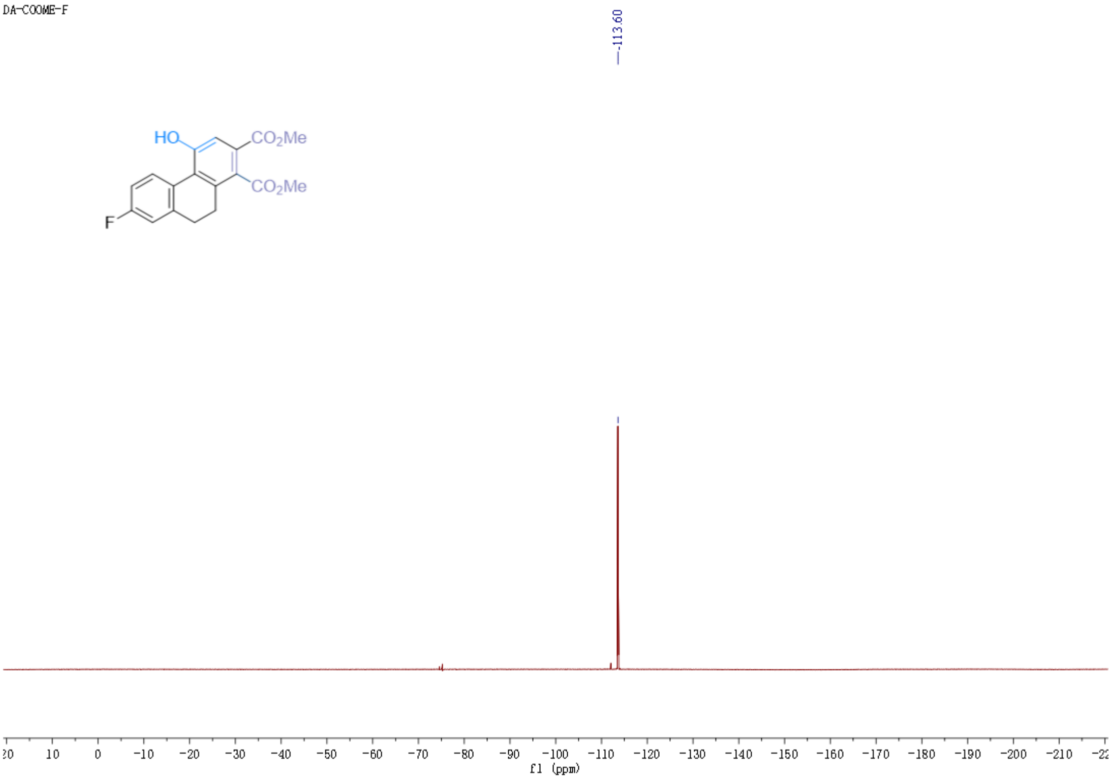


^{13}C NMR spectra of 11c (101 MHz, $(CD_3)_2SO$)



^{19}F NMR NMR spectra of 11c (377 MHz, $(CD_3)_2SO$)



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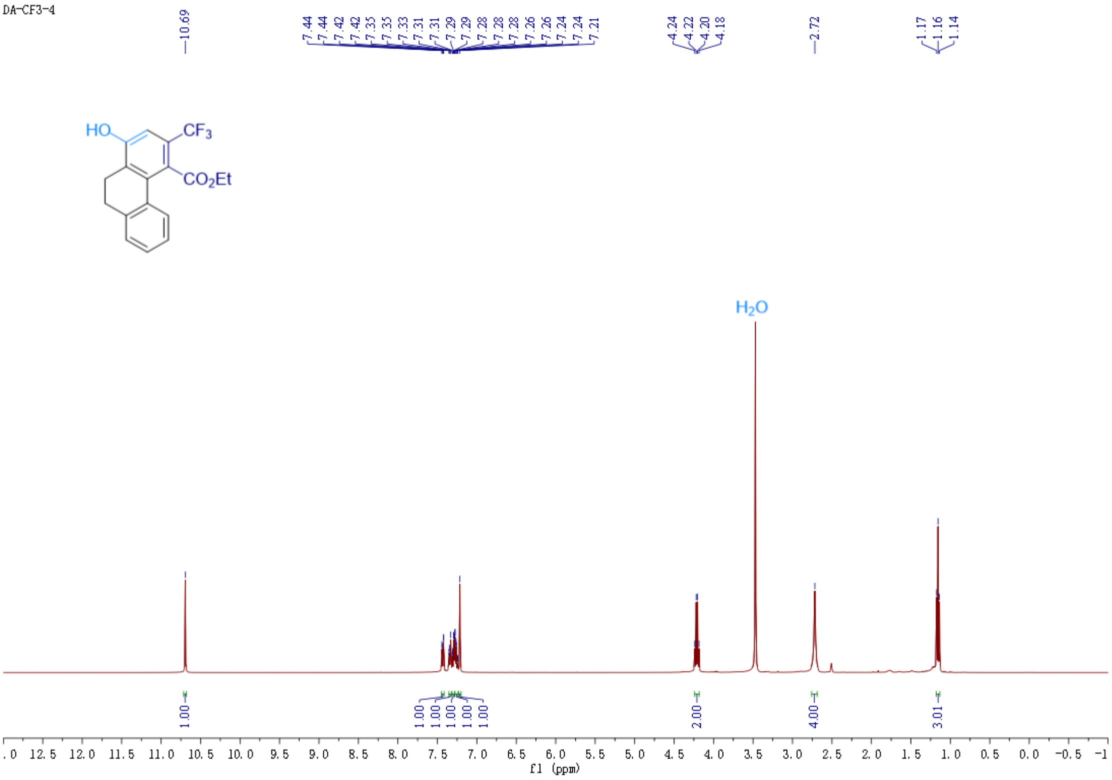
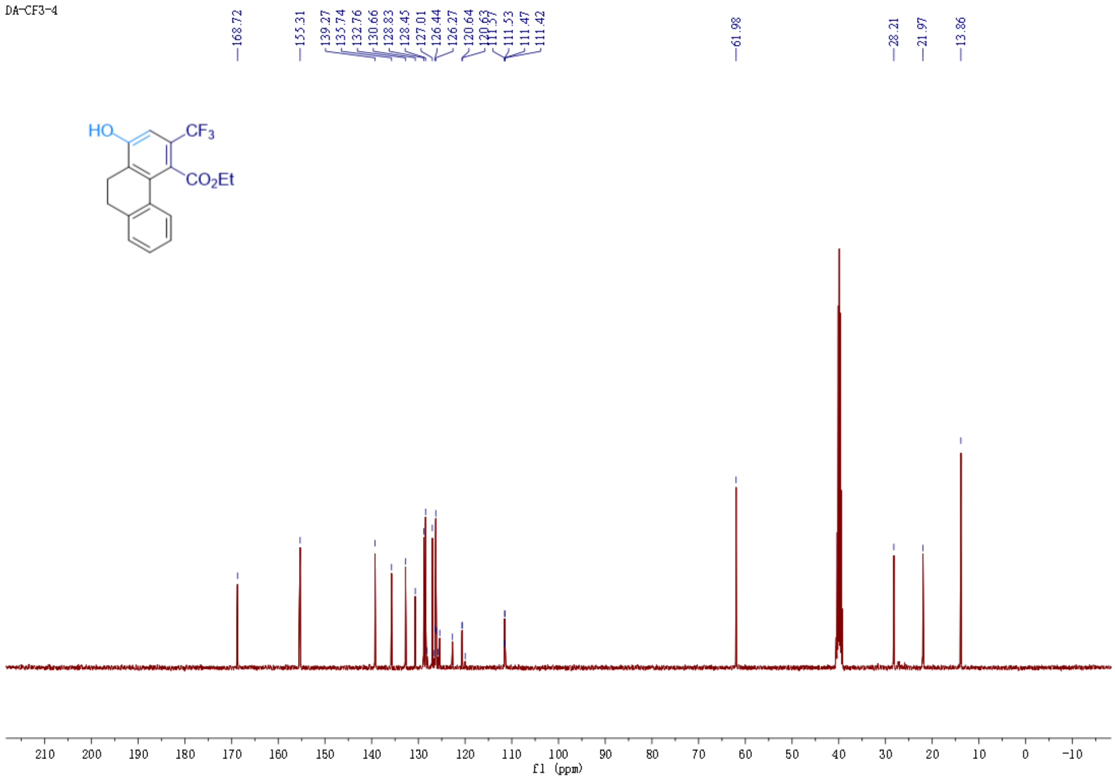
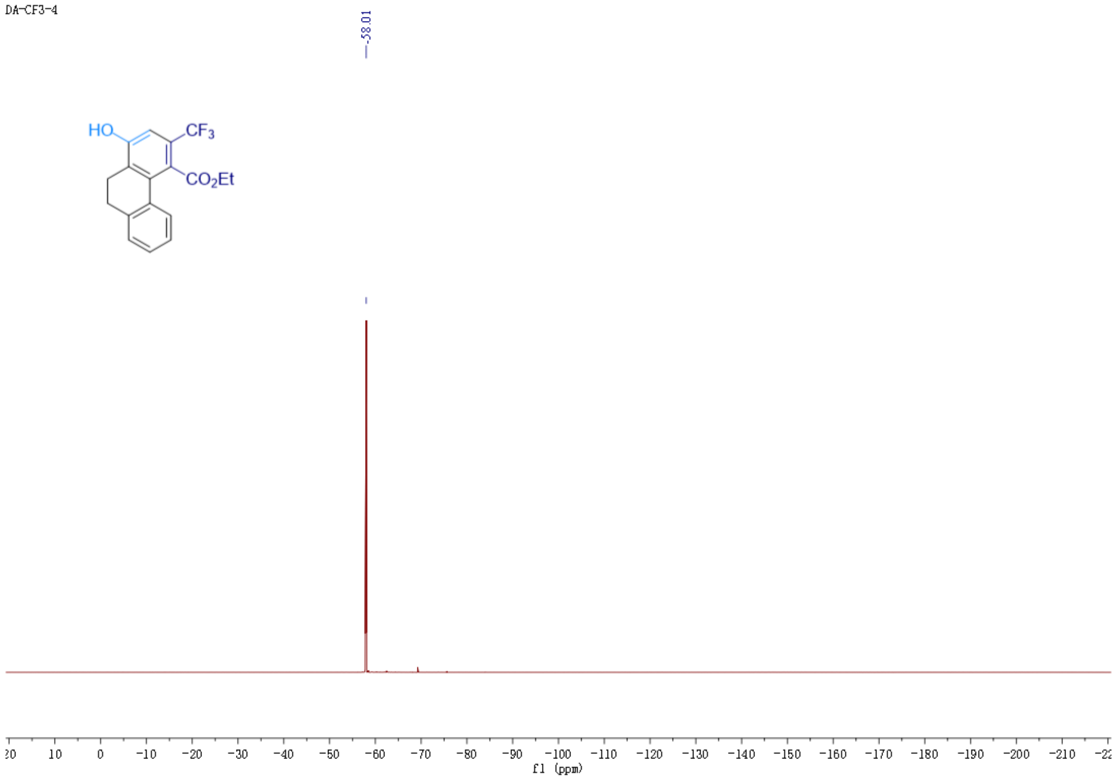


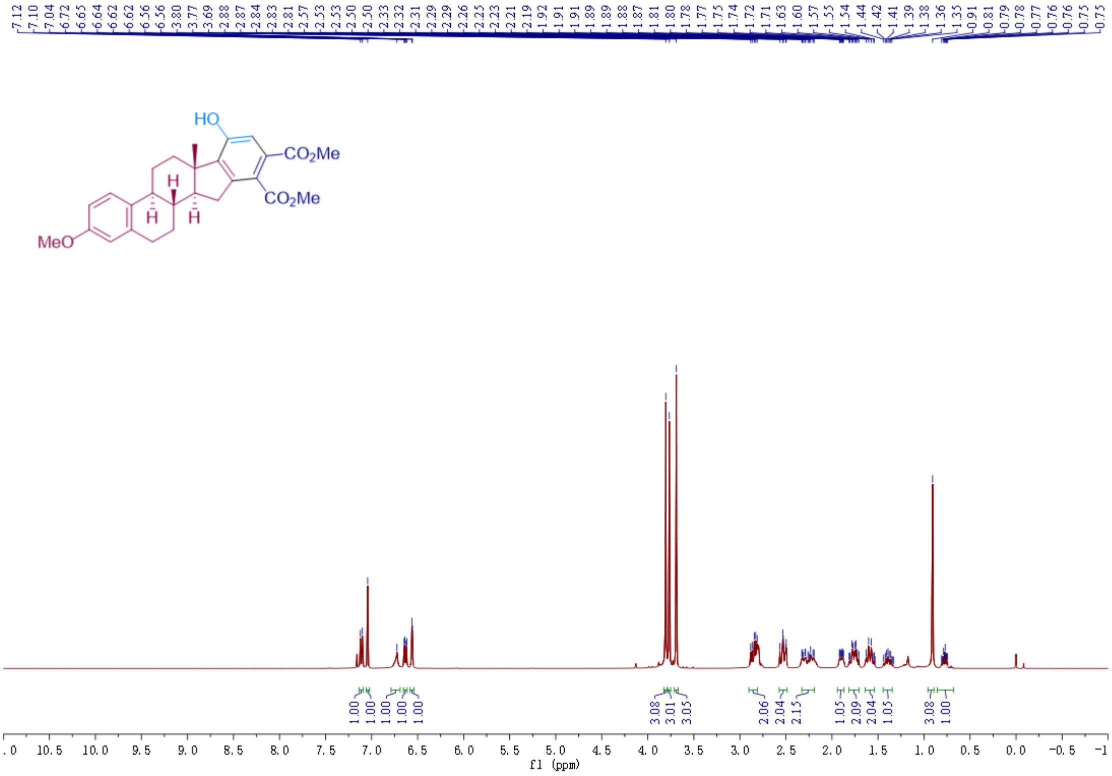
^{13}C NMR spectra of 11d (101 MHz, $(CD_3)_2SO$)



^{19}F NMR NMR spectra of 11d (377 MHz, $(CD_3)_2SO$)



^{1}H NMR spectra of 11e (400 MHz, CDCl$_3$)



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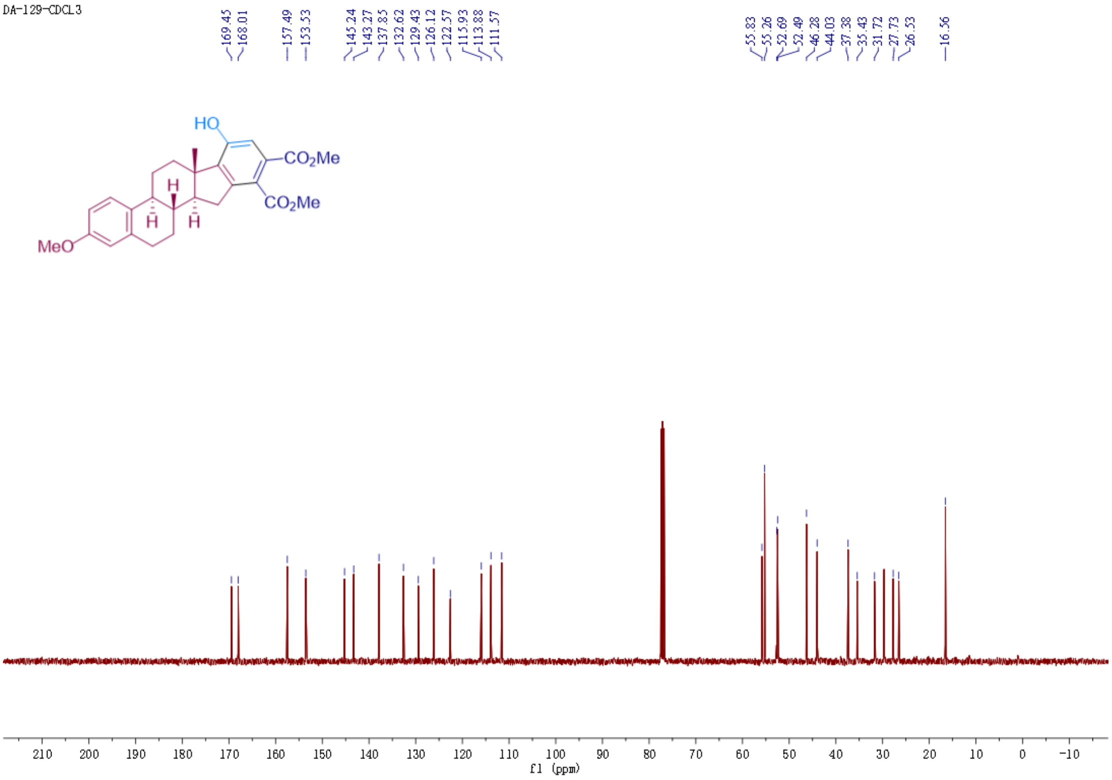
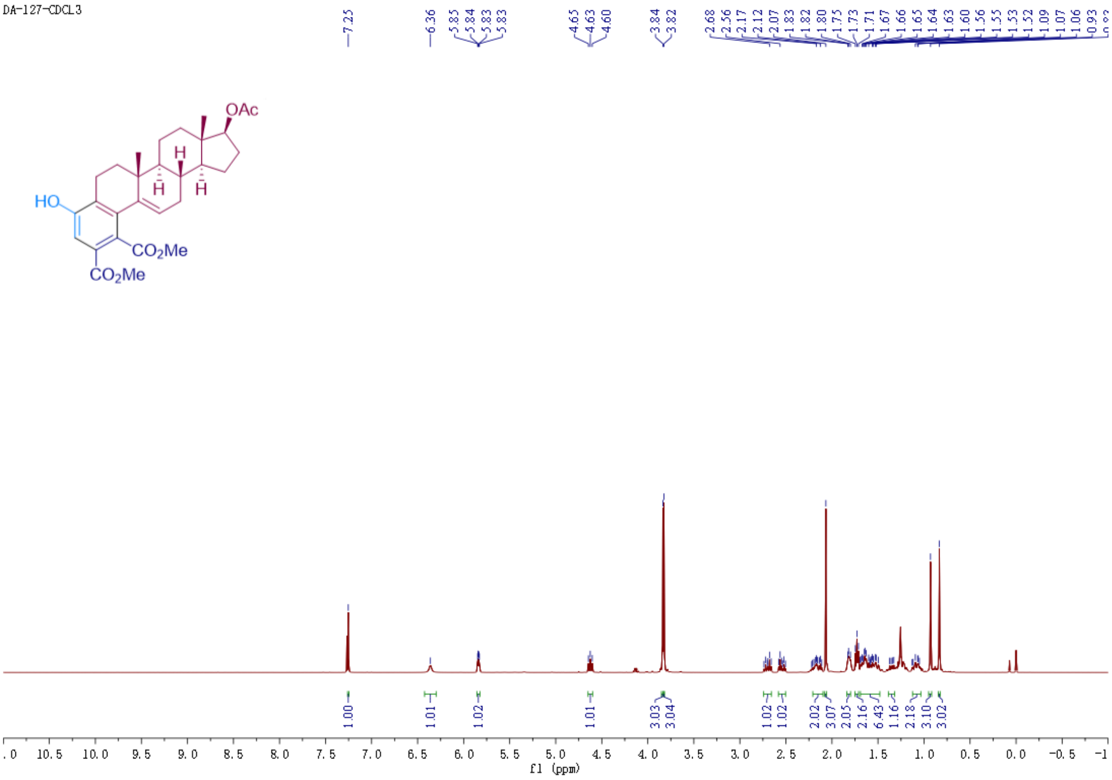
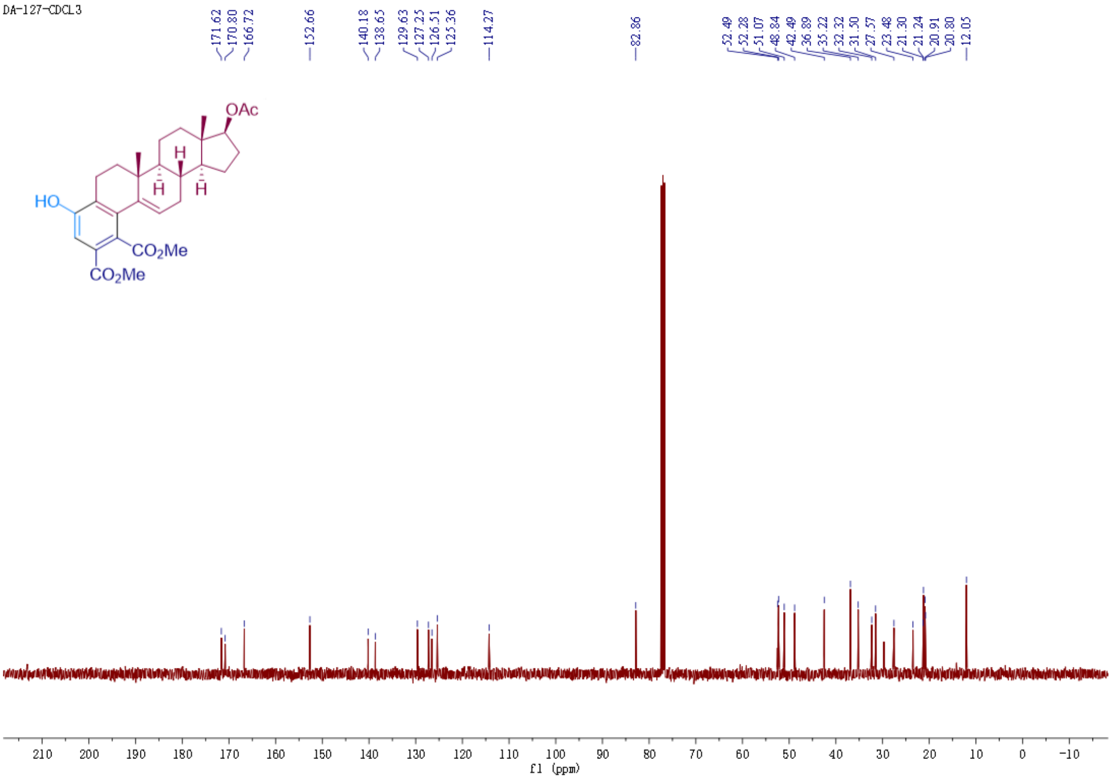


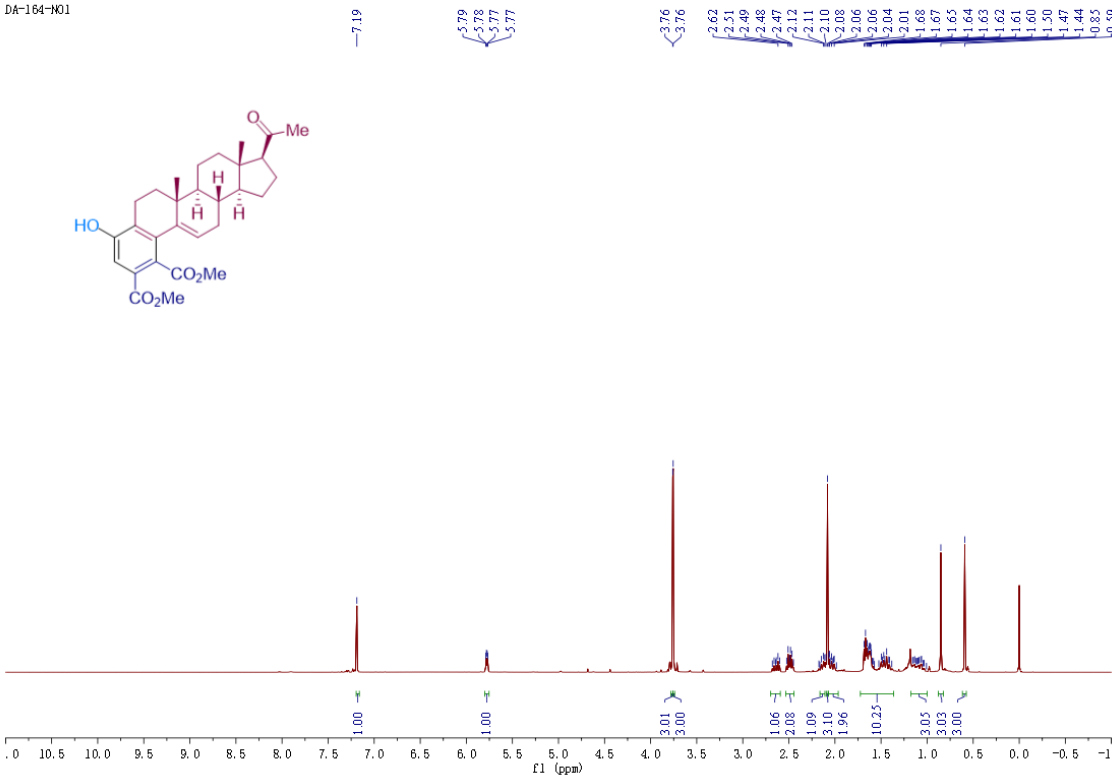
^{1}H NMR spectra of 11f (400 MHz, CDCl$_3$)



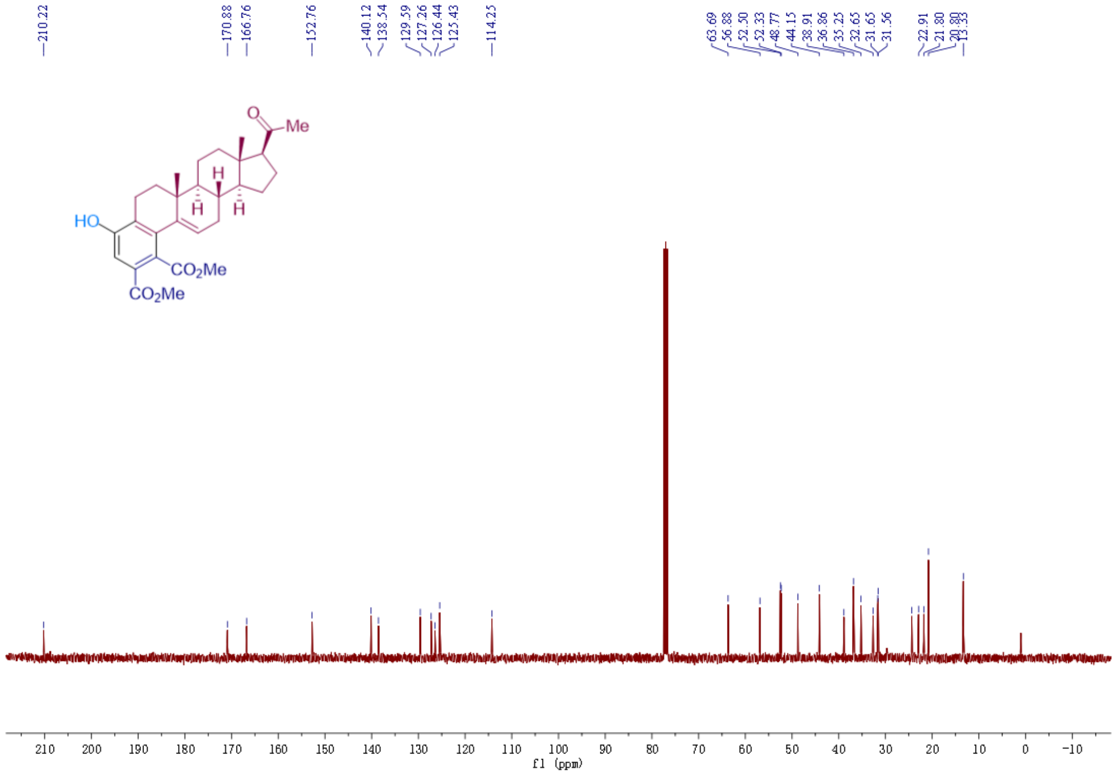
^{13}C NMR spectra of 11f (101 MHz, CDCl$_3$)



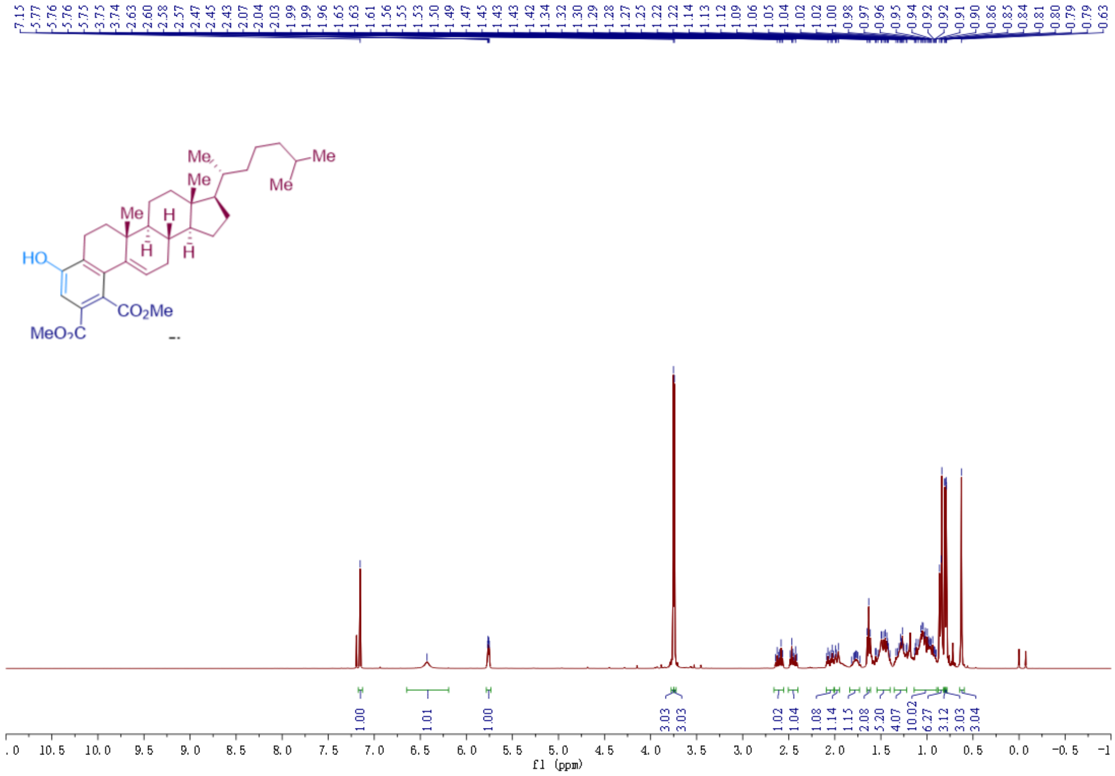
^{1}H NMR spectra of 11g (400 MHz, CDCl$_3$)



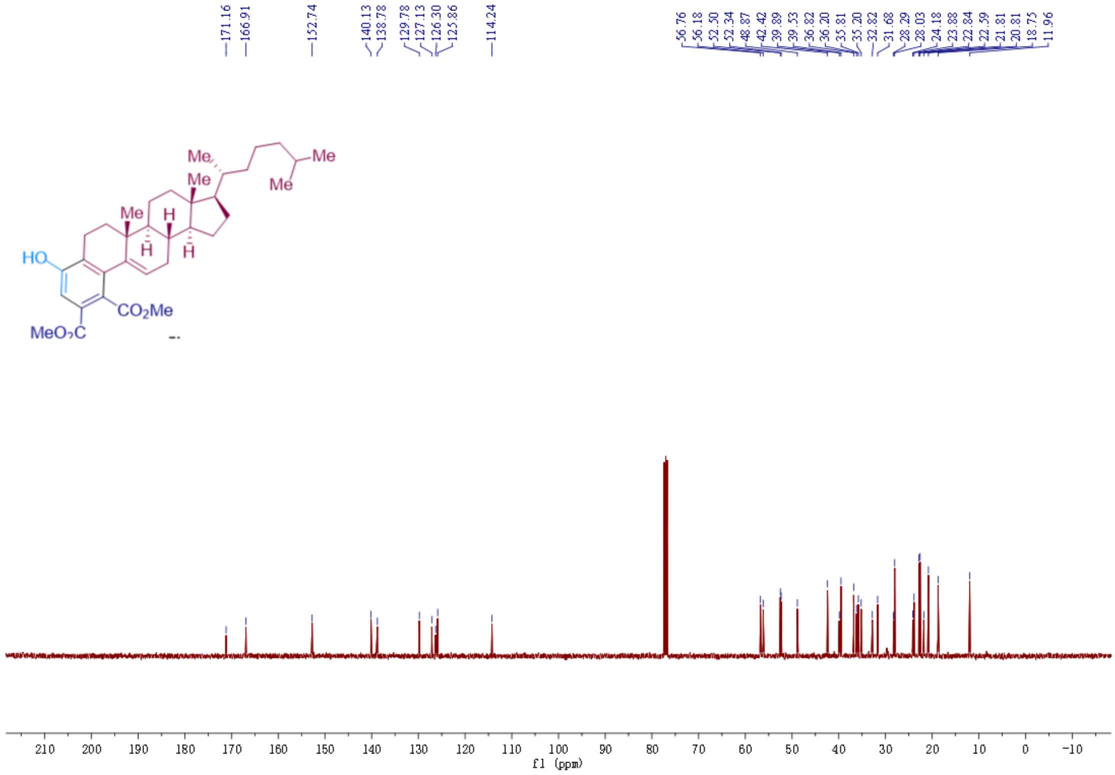
^{13}C NMR spectra of 11g (101 MHz, CDCl$_3$)



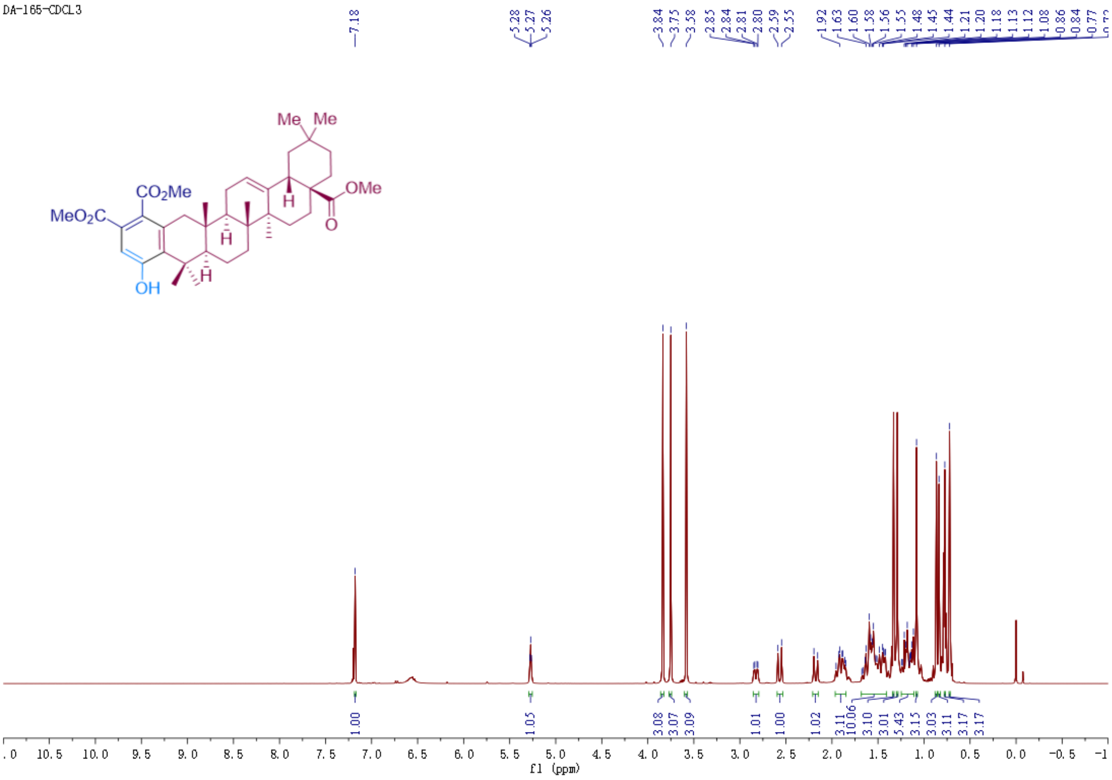
^{1}H NMR spectra of 11h (400 MHz, CDCl$_3$)



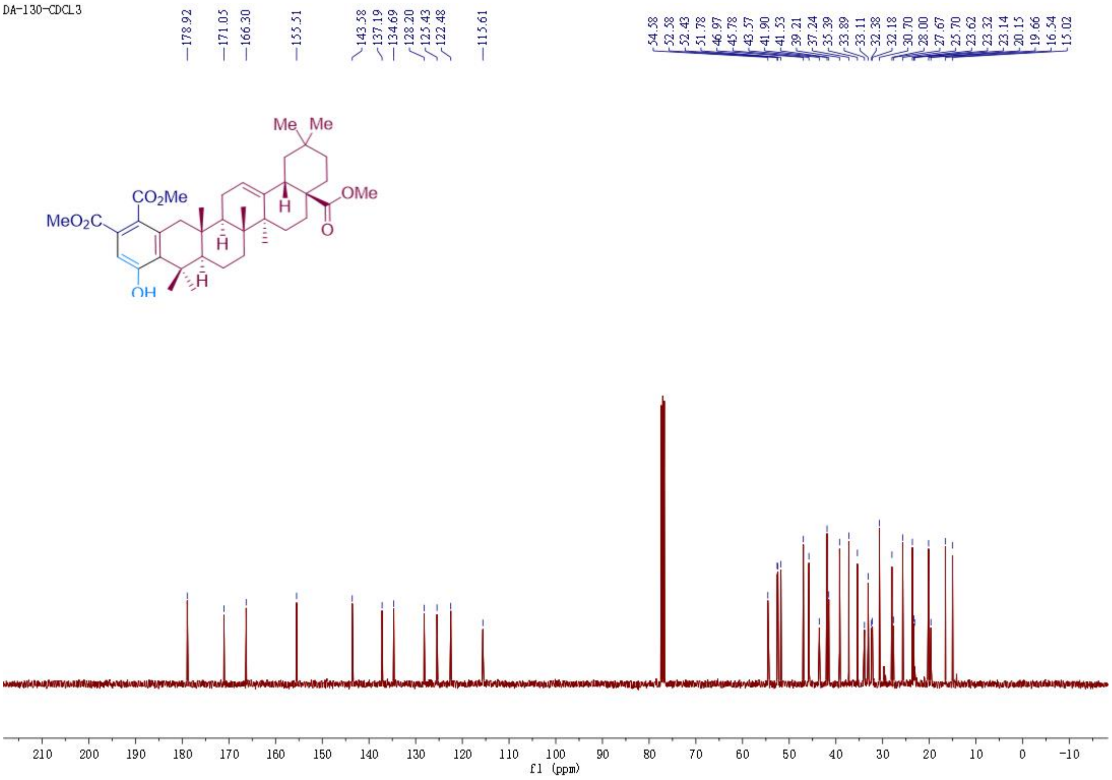
^{13}C NMR spectra of 11h (101 MHz, CDCl$_3$)



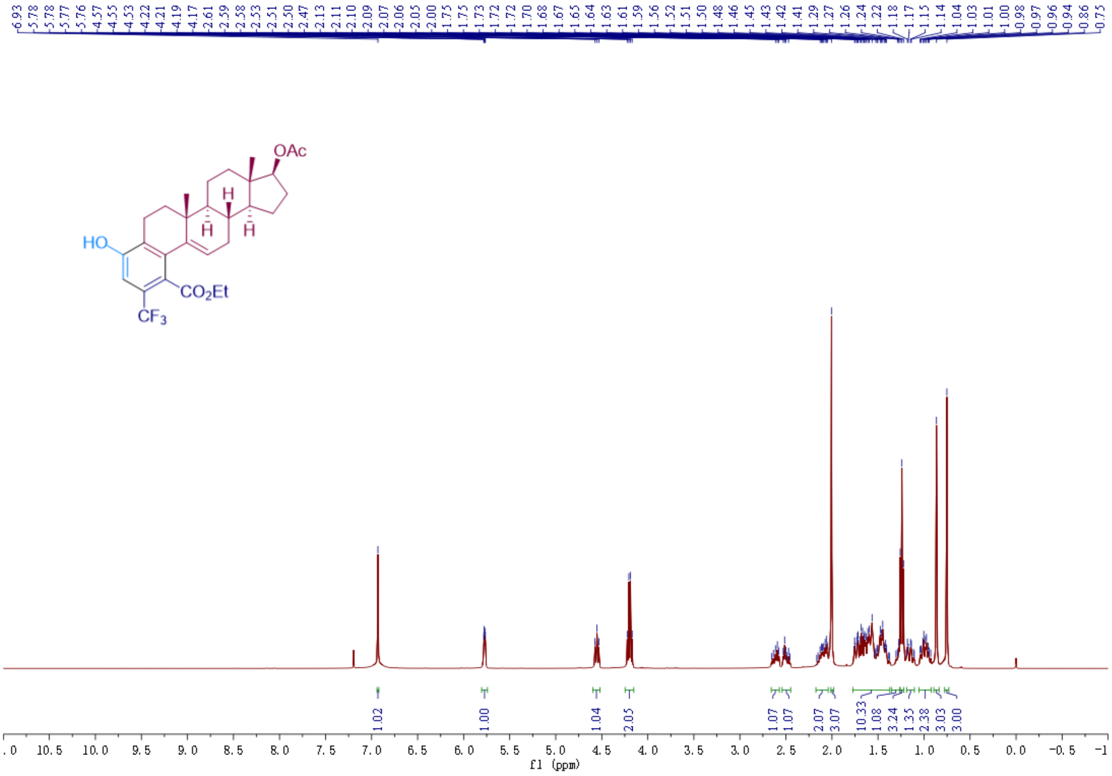
^{1}H NMR spectra of 11i (400 MHz, CDCl$_3$)



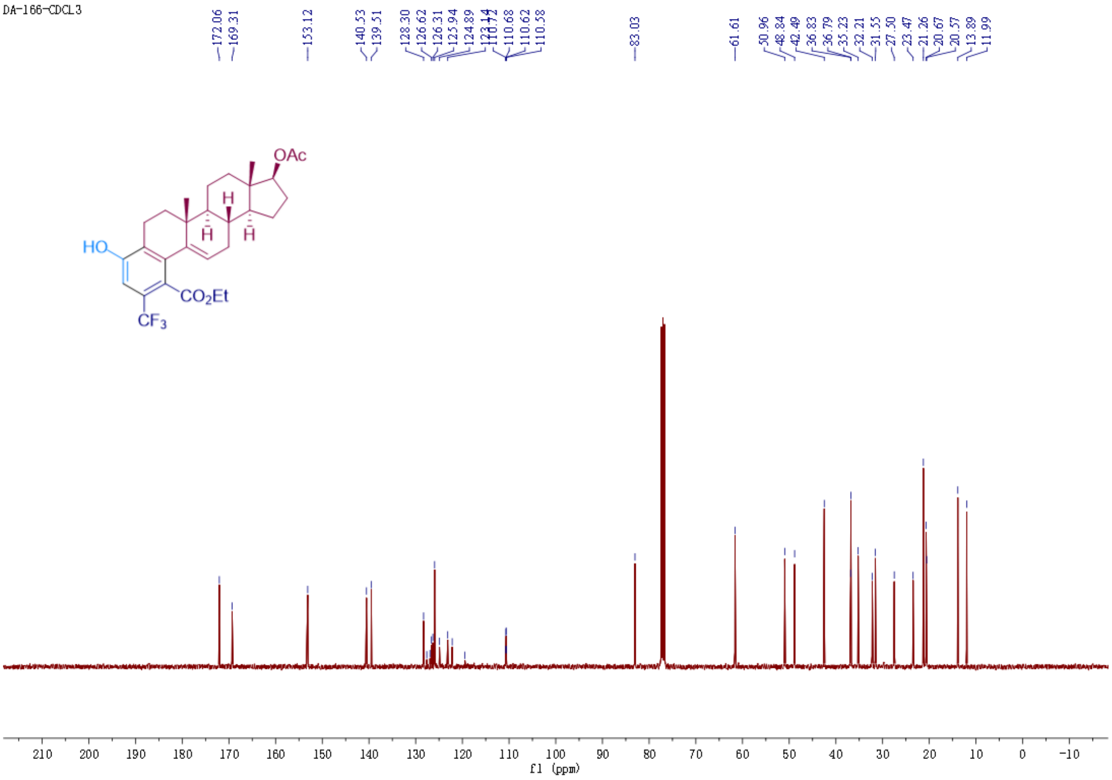
^{13}C NMR spectra of 11i (101 MHz, CDCl$_3$)



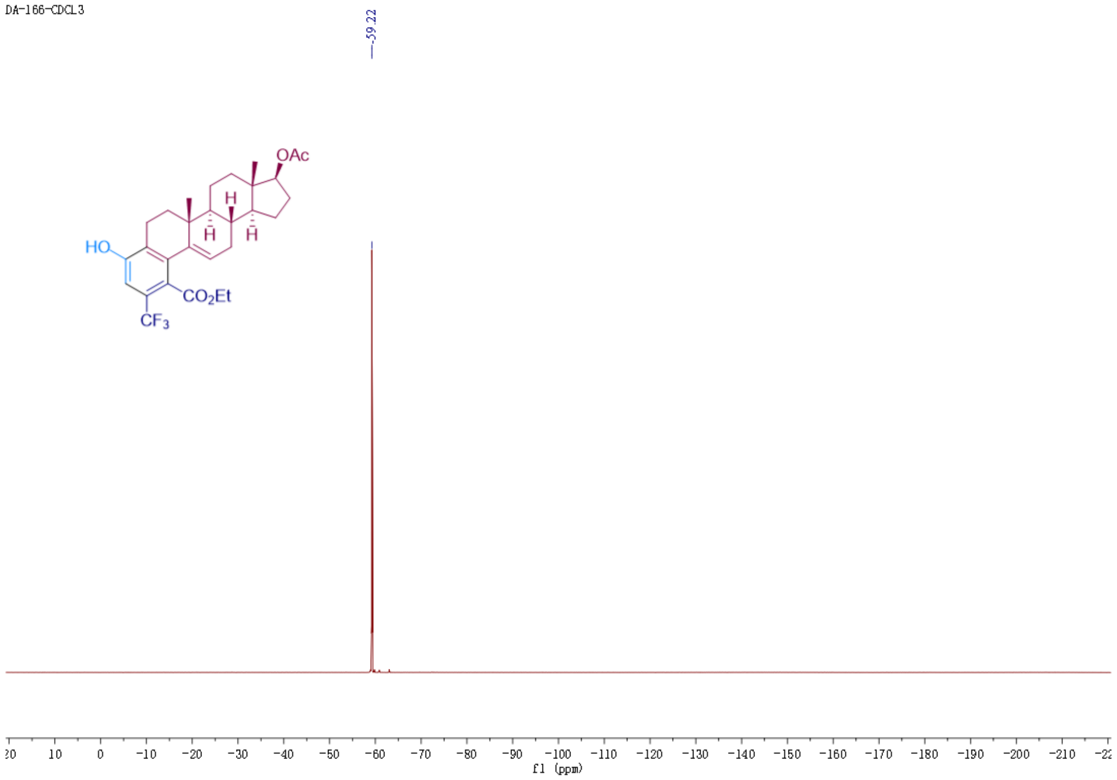
^{1}H NMR spectra of 11j (400 MHz, CDCl$_3$)



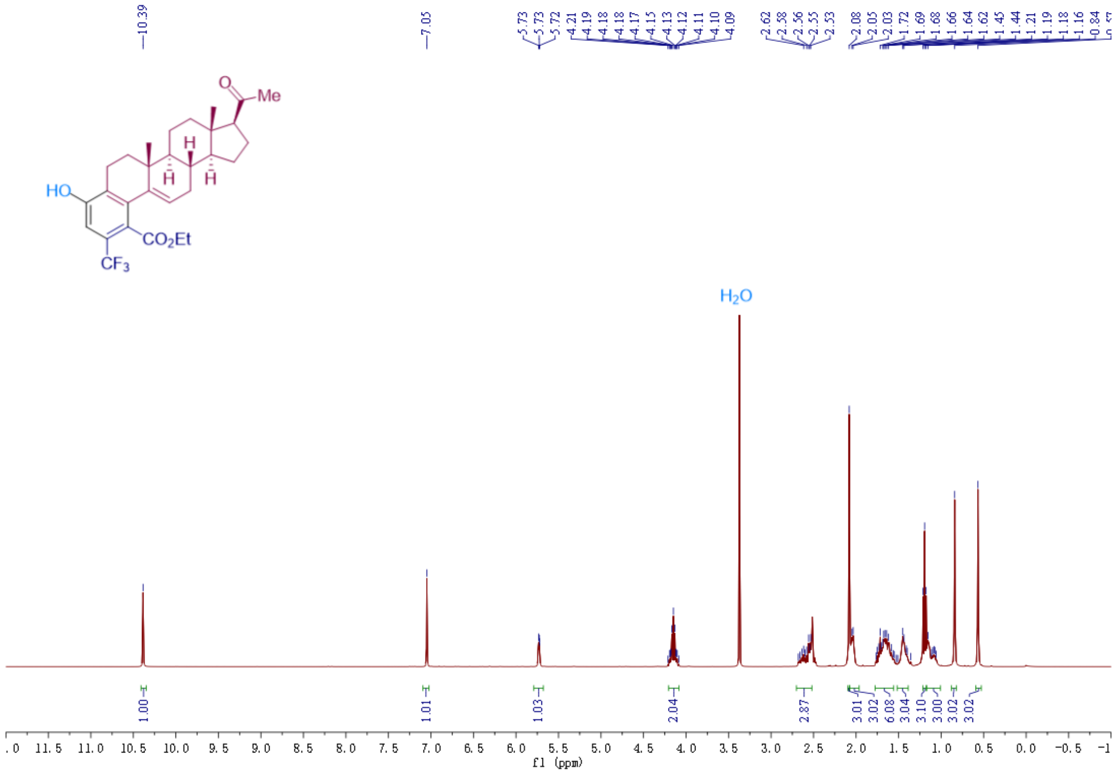
^{13}C NMR spectra of 11j (101 MHz, CDCl$_3$)



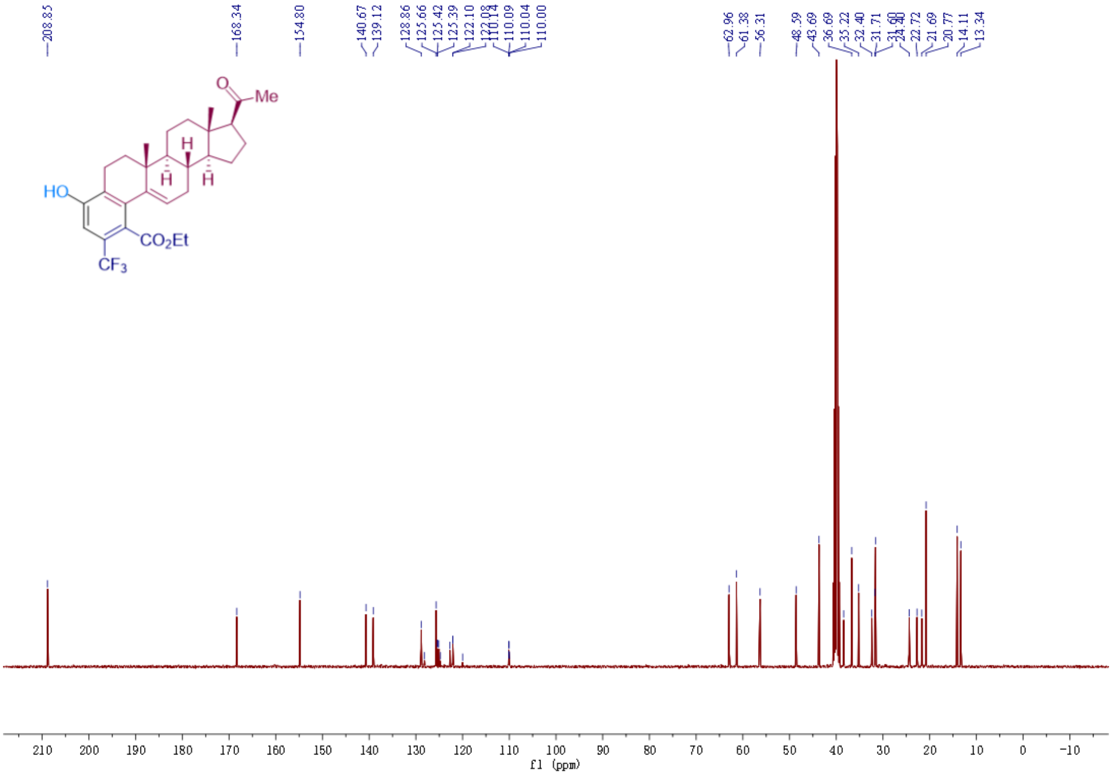
^{19}F NMR NMR spectra of 11j (377 MHz, CDCl$_3$)



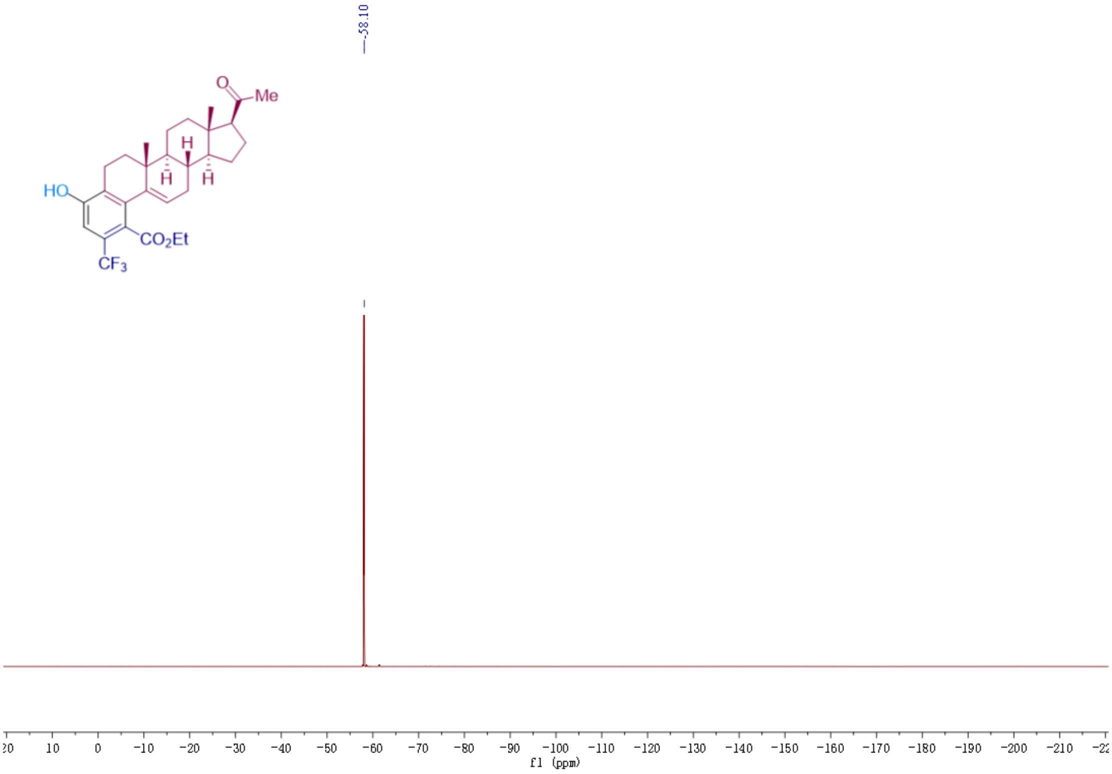
^{1}H NMR spectra of 11k (400 MHz, (CD$_3$)$_2$SO)



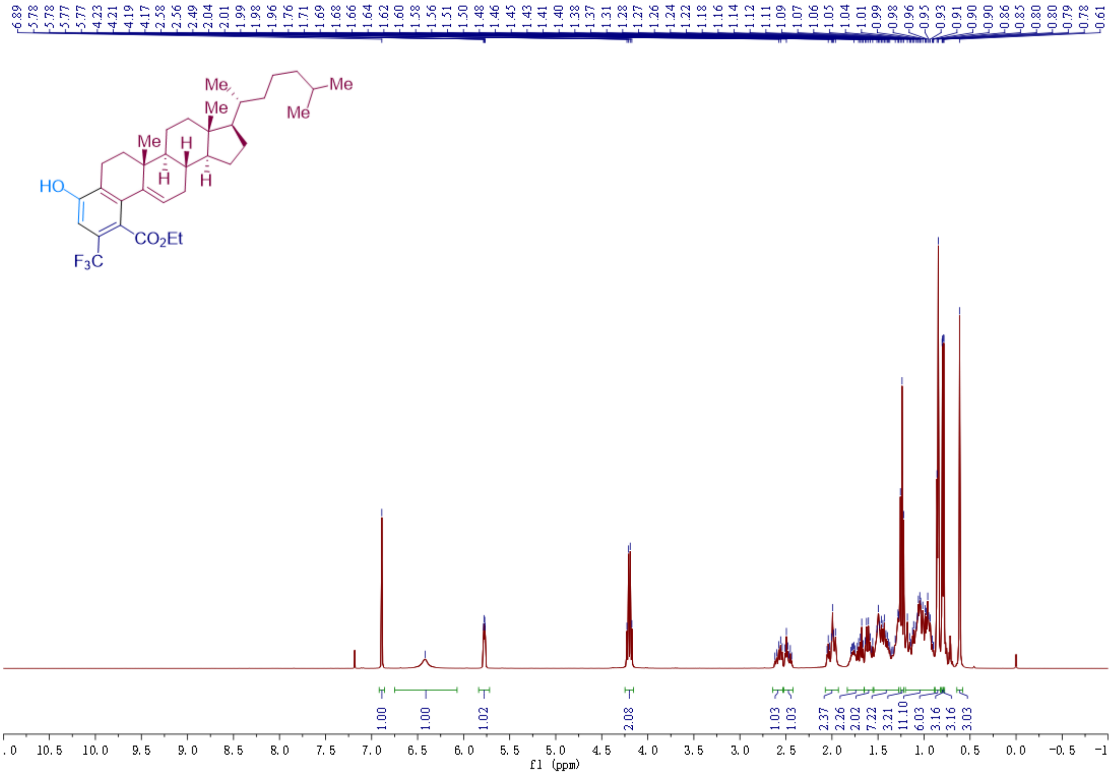
^{13}C NMR spectra of 11k (101 MHz, $(CD_3)_2SO$)



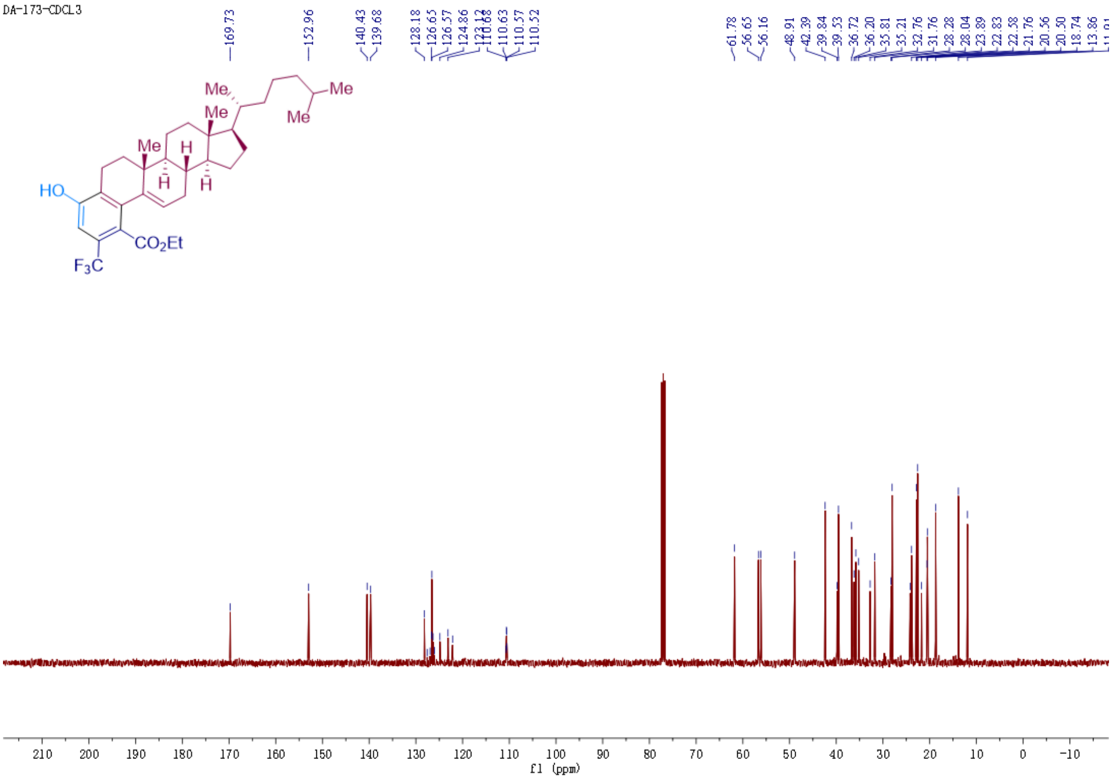
^{19}F NMR NMR spectra of 11k (377 MHz, $(CD_3)_2SO$)



^{1}H NMR spectra of 11l (400 MHz, CDCl$_3$)



^{13}C NMR spectra of 11l (101 MHz, CDCl$_3$)



^{19}F NMR NMR spectra of 11l (377 MHz, $CDCl_3$)